PURIFICATION OF PHOSPHORIC ACID BY SOLVENT EXTRACTION

by

WALEED ANWAR YACU

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TO MY WIFE AND MY PARENTS

SUMMARY

PURIFICATION OF PHOSPHORIC ACID BY SOLVENT EXTRACTION

WALEED ANWAR YACU Ph.D. 1977

This work follows a feasibility study (187) which suggested that a process for purifying wet-process phosphoric acid by solvent extraction should be economically viable. The work was divided into two main areas, (i) chemical and physical measurements on the three-phase system, with or without impurities; (ii) process simulation and optimization. The object was to test the process technically and economically and to optimise the type of solvent.

The chemical equilibria and distribution curves for the system water - phosphoric acid - solvent for the solvents n-amyl alcohol, tri-n-butyl phosphate, di-isopropyl ether and methyl isobutyl ketone have been determined. Both pure phosphoric acid and acid containing known amounts of naturally occurring impurities (Fe PO_4, $AlPO_4$, $Ca_3(PO_4)_2$ and $Mg_3(PO_4)_2$) were examined.

The hydrodynamic characteristics of the systems were also studied. The experimental results obtained for drop size distribution were compared with those obtainable from Hinze's equation (32) and it was found that they deviated by an amount related to the turbulence.

A comprehensive literature survey on the purification of wet-process phosphoric acid by organic solvents has been made. The literature regarding solvent extraction fundamentals and equipment and optimization methods for the envisaged process was also reviewed.

A modified form of the Kremser-Brown and Saunders equation to calculate the number of contact stages was derived. The modification takes into account the special nature of phosphoric acid distribution curves in the studied systems.

The process flow-sheet was developed and simulated. Powell's direct search optimization method was selected in conjunction with the linear search algorithm of Davies, Swann and Campey. The objective function was defined as the total annual manufacturing cost and the program was employed to find the optimum operating conditions for any one of the chosen solvents.

The final results demonstrated the following order of feasibility to purify wet-process acid: di-isopropyl ether, methyl isobutyl ketone, n-amyl alcohol and tri-n-butyl phosphate.

Key Words: PHOSPHORIC ACID PURIFICATION, SOLVENT EXTRACTION

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CHAPTER ONE

INTRODUCTION

Phosphoric acid is an important chemical intermediate used mainly in fertilizers but also in the production of many other chemical products. By far the major outlet for "wet-process" acid is in fertilizers such as triple superphosphate and ammonium phosphate. The purer "thermal" (or "dry") acid is used in detergents and water treatment, catalysis, food and pharmaceutical products, flame proofing, metal treatment and tanning. Although, clearly, a high purity acid is necessary for a number of the above uses, there must be many for which a purified wet-process acid would be suitable if available at a lower selling price than thermal-process acid.

Phosphate rock (mainly fluorapatite) is the raw material for the production of phosphoric acid by both the major routes. The "Thermal" processes are based on the high temperature reduction of the rock with carbon and silica to phosphorus, followed by oxidation to P_2O_5 which is then hydrated to the acid. In the "wet" processes, the rock is first digested with a mineral acid (mainly sulphuric acid) and the product is separated from gypsum by crystallization and filtration.

The difference between manufacturing costs of the wet-process and the thermal process phosphoric acid is substantial (186). This arises from both high energy consumption (about

11000. KWH is used per ton of recovered phosphorus (186)) and more complex processing. In addition, increasing energy costs will tend to make the thermal acid increasingly expensive. This provides economic as well as technical incentive to use purification techniques to produce purer acid from the wet-process route.

Numerous methods (139) have been proposed for purifying wet-process phosphoric acid. These include settling and centrifugation, often with flocculating agents under different operating conditions. Although these operations improve the acid, they do not solve completely the problems of additional sludge formation and the acid end-uses are still limited to fertilizers. Another approach is to extract the acid with an organic solvent leaving the impurities behind in a "dirty" acid fraction.

From a feasibility study comparing various process operations for up-grading of wet-process phosphoric acid (187), a solvent extraction process appeared to be promising and could be economically feasible provided it is technically possible.

The objective for this work, therefore, was to examine in detail the application of a solvent extraction technique for the purification of phosphoric acid. This was divided into the following areas:

I Technically to study the chemical equilibrium and hydrodynamic behaviour of a number of carefully selected solvent systems with water and phosphoric

acid, both pure and impure. The information obtained should be adequate for the design, operation and control of a purification plant.

II Economically, to evaluate and optimize the various purification systems in order to determine the optimum flow-sheet design and operating conditions for each solvent.

Thus, the overall optimum purification plant could be determined. This should test the validity and feasibility of solvent extraction as a technique for the production of pure phosphoric acid from wet-process acid compared with the expensive thermal (dry) method.

CHAPTER TWO

PURIFICATION OF WET-PROCESS PHOSPHORIC ACID BY SOLVENT EXTRACTION

2.1 NATURE OF IMPURITIES

Phosphoric acid obtained by the wet-process contains a wide variety of impurities, dissolved and suspended materials both inorganic and organic. Phosphate rock is the primary source of these impurities. Reagents used for the beneficiation of the rock, sulphuric acid and processing equipment that is chemically and physically attacked during manufacturing steps are the secondary source. Different raw materials and production methods will have a considerable effect on the relative amounts of the impurities.

About 50 chemical elements have been identified in phosphate rocks (77), some of these are present in appreciable amounts, e.g., Fe, Al, Ca, F, Mg and Si. Others are present in very small amounts and these trace impurities include Ba, Sr and V. All these impurities adverseley affect the quality of acid, impart undesired colour and turbidity and change its physical properties and therefore limit its use to applications in which purity is not a critical property.

The major difficulties involved during the manufacture of wet-process acid are thoseof obtaining an easily filterable calcium sulphate and of preventing the formation of sludge in

the acid. These difficulties appear to be caused mainly by a relatively small group of impurities that are present in almost all phosphate rocks. Trace impurities, although present in very low concentrations, have been reported (77) to contribute to processing difficulties. These include suspended colloidal particles that impede filtration or influence the nucleation and crystal growth of calcium sulphate. The instability of dissolved impurities and their tendency towards precipitation are very common problems (78, 79). Some precipitate so rapidly that they hinder the growth of calcium sulphate, reduce the filtration rate and interfere with the recovery of acid from the filter cake. In general most precipitation of the dissolved impurities takes place during the evaporation (concentration) step and continues for days or weeks during storage. The precipitated sludge introduces serious handling and storage problems and loss of available phosphorus. The entire group of important sludge-forming components (Fe, Al, Mg, F, Na, K, Si and SO_3) - occurs in all commercial acids. Furthermore, phosphate ores from different sources contribute these impurities to the wet-process acid in roughly the same relative proportions; but the minerelogical forms in which these impurities occur vary widely from one deposit to another, and these minerals differ considerably in their solubility in the acid. Thus the extent to which these impurities dissolve in the acid is controlled by the chemical composition and solubilities of the individual minerals in which these impurities occur. Beneficiation of the rock substantially reduces the content of nonphosphatic minerals but a significant fraction of the impurities are so

TABLE 2.1 : Representative Composition of some Commercial Phosphate Rock Concentrates (77)

Source & Type	Composition %										
	P_2O_5	CaO	F	CO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	SiO_2	SO_3
Florida											
Land pebble	30-36	46-50	3.3-4.0	1.5-4.4	0.7-1.1	0.7-2.6	0.04-0.5	0.09-0.5	0.07-0.6	7.3-9.8	0.5-1.5
Hard rock	33-36	49-51	3.4-3.9	1.8-2.8	0.5-1.4	0.7-1.3	0.03-0.2	0.06-0.3	0.1-0.4	4.3-6.4	0.1-0.6
Tennessee											
Blue rock	28-33	43-49	3.3-3.8	0.9-2.6	0.6-1.2	1.8-3.5	0.07-0.4	0.04-0.6	0.1 -0.4	4.9-12.4	4.0-7.1
Brown rock	32.8-37.5	45.3-50.8	3.4-4.0	1.1-3.7	1.2-2.7	0.9-3.4	0. -0.2	0.2- 0.4	0.1 -0.3	1.9-8.1	0.4-0.8
Wyoming	30.2	46.2	3.54	4.13	1.2	0.87	0.1	0.35	0.64	7.2	1.35
North Carolina	30.2-30.3	48.6-49.7	3.5-3.8	5.4-5.8	0.5-0.6	0.6-0.7	0.5	0.11	0.9- 1.0	2.3-3.6	0.98
Morocco	32.8-37.2	51.8-54.2	3.5-4.2	2.6-4.6	0.3-0.4	0.1-0.5	0.1 -0.5	0.10	0.3- 0.8	1.0-2.4	0.6-1.6
Algeria	30.1	50.1	2.65	6.70	0.20	0.35	0.90	0.08	1.53	2.13	2.4
Togo	37.29	51.71	3.32	1.27	0.67	1.60	0.1	0.03	0.12	3.35	0.24
Igneous apatite Quebec	40 -40.6	52.4-55.5	3.3-3.4	0.3-1.5	0.6		0.5			0.5-3.1	
Kola	39.0	52.2	3.20	0.2	0.79	0.68	0.1	0.28	0.77	2.4	nil

TABLE 2.2 : Composition of Filtered Wet-Process Phosphoric Acid (77)

Rock Source	Acid Composition%									
	P_2O_5	CaO	F	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	SiO_2	SO_3
Florida[a]	27.3	0.15	1.7	0.6	1.1	0.28	0.03	0.08		1.2
Florida[b]	28.4	0.1	1.5	1.1	2.0					3.9
Florida[c]	30.0	1.26	2.36	1.08	0.86		0.06	0.01	1.21	3.72
Western U.S.[a]	23.2	0.22	1.2	0.8	0.6	0.33	0.05	0.13		1.0
Tennessee[c]	30.0	0.37	2.54	2.66	2.27		0.07	0.43	0.1	1.49

[a]Composition of clear, supernatent acid after cessation of precipitation.

[b]Composition of acids include any suspended solid material in shipped acid.

[c]Data taken from Table II of Hill (120) and recalculated (77) to 30% P_2O_5. basis for comparison

TABLE 2.3 : Composition of Concentrated Wet-Process Phosphoric Acids (77)

Rock Source	Composition %									
	P_2O_5	CaO	F	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	SiO_2	SO_3
Florida	53.1	0.20	0.5	1.32	1.72	0.32	0.01	0.30	0.7	1.5
	50.8	0.1	0.6	1.13	1.23	0.40	0.04	0.08	0.7	2.8
	57.7	0.03	0.3	1.0	1.8	0.36	0.004	0.04		3.2
	56.3	0.15	0.4	1.7	1.2	0.50	0.009	0.04		2.0
Western U.S.	41.7	0.06	1.4	1.8	1.6	0.15	0.018	0.03		1.4
	51.2	0.04	0.5	1.51	0.72	0.30	0.08	0.09	0.6	2.3
Tennessee[a]	54.0	0.02	2.58	3.90	2.62		0.02	0.01	0.86	1.9

[a]Data taken from Table II of Hill (120) and recalculated (77) to 54% P_2O_5 basis for comparison purposes

intimately associated with the mineral apatite that they cannot be removed by physical beneficiation methods. The composition of typical phosphate rock concentrates is shown in Table 2.1, filtered wet-process acid in Table 2.2 and concentrated wet-process acid in Table 2.3.

2.2 THEORY OF EXTRACTION OF MINERAL ACIDS

In general the extraction of a covalent molecule from aqueous solutions is possible with essentially any organic solvent which is immiscible with water, although specific effects modify the distribution coefficient in certain cases. Small ionic species, however, are relatively strongly solvated in aqueous solutions by the highly polar water molecules to an extent depending on their physical and chemical properties. Therefore, it is very difficult for them to extract into non-polar, non-coordinating solvents which cannot compensate for the resulting loss of hydration energy. Only those solvents which can provide primary solvation and/or a high dielectric medium may overcome the forces which hold these ionic species in water (81).

When the molecules of a substance are polar, they exhibit a dipole moment caused by unequal sharing of the electrons of the covalent bonds of the molecule. For example, in the case of an alcohol molecule (17), the electron pair that makes up the bond between oxygen and hydrogen lies closer to the oxygen:

$$R - \overline{O}: \quad H^{+}$$

Consequently, the hydrogen portion of the molecule is relatively positively charged and the remainder is negatively charged, and the dipole moment is used as a measure of this phenomenon. Polar molecules tend to associate with coordination of hydrogen between the negative parts of adjacent molecules:

$$\begin{array}{cccccccc} & R & & R & & R & & R \\ & | & & | & & | & & | \\ H - O & \rightarrow & H - O & \rightarrow & H - O & \rightarrow & H - O \end{array}$$

Hydrogen can also coordinate between other donor atoms such as nitrogen or fluorine as well as oxygen.

Solution of solute into a solvent which takes place through hydrogen bonding may involve either breaking the hydrogen bonds or forming new ones. Thus, for example, if an alcohol dissolves in water, the hydrogen bonds between the water molecules and between the alcohol molecules may be broken and new bonds formed between alcohol and water molecules as shown below

$$\begin{array}{cccccccc} & H & & R & & H & & R \\ & | & & | & & | & & | \\ H - O & \rightarrow & H - O & \rightarrow & H - O & \rightarrow & H - O \end{array}$$

Ewell, Harrison and Berg (80) classified liquids into five groupings based on their possibilities of forming hydrogen bonds. These are -

Class I : Liquids capable of forming three-dimensional networks of strong hydrogen bonds, e.g. water, glycol, glycerol, amino alcohols, etc.

Class II : Liquids composed of molecules containing both active

hydrogen atoms and donor atoms (oxygen, nitrogen, and flourine) e.g. alcohols, acids, phenols, primary and secondary amines, etc.

Class III : Liquids composed of molecules containing donor atoms but no active hydrogen atoms, e.g. ethers, ketones, aldehydes, esters, tertiary amines, etc.

Class IV : Liquids composed of molecules containing active hydrogen atoms but no donor atoms, e.g. $CHCl_3$, CH_2Cl_2, CH_3CHCl_2 etc.

Class V : All other liquids, i.e. liquids having no hydrogen bond forming capabilities, e.g. hydrocarbons, carbon disulphide, sulphides, etc.

From the above classification it is clear that some organic solvent molecules have the ability to form hydrogen bonded complexes. Since water itself can bind to other water molecules and to other suitable species by hydrogen and/or induced dipole interaction, suitable organic solvents must compete with water in a two-phase system containing ions which are to be solvated for the coordination with these ions. If the properties of the organic phase are suitable, the result may be the formation of a complex species which is sufficiently solvated by the non-aqueous solvent to allow it to pass into the organic phase. This is in contrast with the behaviour of molecular species for which, in general the chemical nature of the solvent is not a critical factor (81).

Many organic solvents possess functional groups which confer basic properties upon the parent molecule, and oxygenated

solvents such as ethers, ketones, and esters have such properties. The evidence for the formation of hydrogen-bonded complexes between basic solvents and mineral acids was probably first interpreted by Sutton (82) for the extraction of nitric acid into diethyl ether in terms of the equilibriums:

$$HNO_3 + (CH_3CH_2)_2O = (CH_3CH_2)_2O.\ HNO_3$$

later, Glueckanf (83) pointed out that the formation of such complexes is a common feature of all ternary systems involving ethers in equilibrium with nitric acid and water.

Brown and Mathieson (84) have re-examined the published data on the extraction of chloroacetic acids and found that the extraction was affected by the dimerization of the acid in the organic phase and the possibility of interaction between the acid monomer and the solvent. In nonhydrogen-bonding solvents of low dielectric constant these acids exist largely as dimers and in any given solvent of this type the more highly chlorinated acids are the more highly associated. With a basic solvent, the ability to interact with the acid by hydrogen bonding brings about the dissociation of the dimers. The more highly chlorinated acids, which are the stronger acids, form stronger hydrogen bonds with basic solvents. This treatment emphasises the importance of solvation in the organic solvents in the extraction of acidic species.

It is worth noting the effect of basicity on the solubility of water in organic solvents (85). The solubility of hydrocarbons in water is typically equivalent to a mole fraction of $10^{-3} \rightarrow 10^{-4}$;

in ethers, on the other hand, the solubility is orders of magnitude higher than this and in the case of strongly basic phosphoryl compounds, the solubility of water corresponds to complete formation of a 1:1 complex such as Trin-butyl phosphate (TBP). H_2O (86, 87). In the presence of concentrated nitric acid and a diluent in TBP this system becomes more complicated (88) due to the formation of a TBP.HNO_3 complex as a third phase. The appearance of this third phase was not obtained when phosphoric acid was used instead of nitric acid in this work but a third phase was observed when di-isopropyl ether was used as the solvent. This was confirmed in earlier work by Schallert and Fite, Jr. (89, 90) on the purification of phosphoric acid using di-isopropyl ether and diethyl ether. The phosphoric acid-ether complex formed in both cases was claimed to be accompanied by a molecule of water as expressed by the chemical formulas, $H_3PO_4.H_2O.(CH_3)_2CHOCH(CH_3)_2$, with di-isopropyl ether and $H_3PO_4.H_2O.(CH_3CH_2)_2O$ with diethyl ether. Both complexes are insoluble in dilute aqueous phosphoric acid solutions or in excess ether.

Confirmation of hydrogen bonding in such systems by physical methods has been reported in few cases. The ultraviolet spectrum of nitric acid - butylether extract was investigated by Vdovenko et al (91) who found spectral changes corresponding to hydrogen bonding. Changes have been noted in the infrared spectrum of dibutylcarbitol in the presence of nitic acid (92), and of tri-n-butyl phosphate on the addition of one molar equivalent of water (88).

From studies of viscosity, density, surface tension and the electrical conductivity of binary systems of phosphoric acid with certain aldehydes, amides and ketones (103, 104, 105) Krupatkin and Bratuschehak confirmed the formation of a 1:1 complex compound between phosphoric acid and the solvent with all the solvents they studied. In addition, a compound with a 2:1 ratio of acid to solvent was formed in small amounts in some cases. Analysis of the electrical conductance data showed that some of the complex compounds formed were highly dissociated such as those formed with dimethylacetamide and salicylamide, others were weakly dissociated such as those formed with furfural, benzenophenone and cyclohexanone. While the compounds formed with benzenaldehyde and methyl ethyl ketone behaved as none electrolytes.

Because of its weakness, nitric acid was claimed (81) to extract into organic solvents better than other mineral acids which have been studied presumably because it shows appreciable covalent character in its pure state. With ethers and ketones the same source (81) claimed that the extraction of hydrogen chloride and bromide is poor, with values of the distribution coefficients (D) typically around 0.02, with alcohols, D increases ten-fold, reflecting the stronger solvating properties of these solvents (93). Tributyl phosphate extracts the hydrogen halides to about the same extent as the higher alcohols (94). It was concluded (81) from the solubility of basic organic solvents in hydrogen halide aqueous solutions (95), that the hydrogen halides do interact with the solvents, but that the resultant complex

does not readily extract into the organic phase.

Sulphuric acid was claimed (81) not to be extractable by ketones, ethers and esters, but to extract into alcohols (92, 96). Phosphoric acid was claimed not to be extracted into di-isopropyl ketone. These observations were explained by the fact that both sulphuric and phosphoric acids have strong primary hydration in aqueous solutions and extraction into alcohols is possible only because alcohols can solvate the anions, where with nonhydroxylated solvents the acids strongly favour the aqueous phase. The observations noted above regarding phosphoric acid were in agreement with experimental results achieved in this work only at low concentrations of the acid in both di-isopropyl ether and methylisobutyl ketone. When the acid concentration exceeded a certain threshold level, the distribution of acid increased sharply to an extent that the mentioned solvents extracted the acid even better than n-amyl alcohol and tri n-butyl phosphate at similar high acid concentrations. Similar findings are given in references (97 - 102). Certainly this contradicts with the explanations quoted by Diamond and Tuck (81) and other factors must be predominating at high acid concentrations.

Information on the chemical state of the extracted acid species in the organic phase suggested (81) that the acid is usually accompanied by one or more molecules of water (hydrated). Further investigation is needed before a satisfactory picture of the solvation process of mineral acids in the organic phase is obtained.

Seaton and Geankoplis (106) studied the effect of pH, activity coefficient and internal pressure of the aqueous solution on the extraction of phosphoric acid. They concluded that pH should play an important part in the extraction of a partly ionized acid like phosphoric acid. When the pH value was increased from 0 to 10 the distribution coefficient of the phosphate ion dropped by a factor of 1:100. But since, by changing the pH (by addition of HCl and NaOH) new chemicals (phosphate salts) are formed which behave completely differently from the acid in their solubility in the organic phase, this justification of pH effect becomes rather confusing. The distribution coefficient of phosphoric acid increased when HCl was added, this was explained by the theory that since HCl lowers the internal pressure of water, it diminishes the activity of water towards the acid and hence the organic phase is able to share a greater amount of the acid. Further support for the theory was proposed when HI was added instead HCl. The distribution coefficient increased further but since the activity coefficient of HI in water is higher than that of HCl at the same concentration this was claimed to be a possible contributing factor. The addition of H_2SO_4 was claimed (99) to have a similar effect on the distribution coefficient of H_3PO_4 although H_2SO_4 as well as other mineral acids distribute between the water and the solvent. The activity coefficients of hydrochloric acid were measured (106) in the presence of phosphoric acid. The data showed that the presence of approximately 10% phosphoric acid in aqueous solutions containing 2 to 5% hydrochloric acid raises the activity coefficient of HCl a maximum of only 0.9%, while the

distribution coefficient of HCl increases by 40%. Since the value of the distribution coefficient (D) is directly proportional to the activity coefficient as shown in equation 2.1, it was concluded that changes in internal pressure of water or other factors are causing the increase in the distribution coefficient,

$$K = \frac{a_o}{a_w} = \frac{\gamma_o C_o}{\gamma_o C_w} = \left(\frac{\gamma_o}{\gamma_w} \right) . D \qquad (2.1)$$

where the symbols are described in the nomenclature.

Grinberg and Lozhkina (107) quoted that extraction of acids with organic solvents involves two main procedures; the use of salting out agents and complex compound formation. The first consists of adding salts to the aqueous phase which assist the extraction of acid into the organic phase. Such agents were claimed to act mainly by binding water and thus reducing its concentration as available solvent. The second procedure is because of the capability of mineral acids to form complex compounds with organic solvents as mentioned earlier. These compounds were called by Grinberg and Lozhkina (107) "oxonium compounds". The formation of these oxonium compounds (107) depends on the strength of the acid and the base (organic phase) and if this plays a decisive factor in the extraction of acids into the organic phase, then stronger acids should be better extracted by a given solvent than weaker ones. Yet this is not true and hence, the solubility of these compounds in the organic phase must also be taken into account. Zharovskii and Melnik

(108) showed that the capacity of certain solvents (with the exception of ether and esters for HNO_3) for dissolving acids fall into the following order: diethyl ether < isopentyl acetate < isobutyl acetate < benzyl alcohol < isopentyl alcohol < butanol. This was in agreement with the increasing dielectric constant for these solvents, being 4.335, 4.63, 5.29, 11.5, 14.7 and 17.1 respectively.

The effect of a salting-out agent on the extraction of nitric acid by isoamyl alcohol was demonstrated by Grinberg and Lozhkina (107) by adding calcium nitrate which is soluble in the aqueous phase. The distribution coefficient of the acid increased with the increase of $Ca(NO_3)_2$, and at a constant level of salting-out agent, the acid with higher concentration gave higher distribution coefficient. This case (as well as the case of no salting-out agents) was justified because of the decrease in the dissociation of the acid as its concentration in the solution increases. Values of distribution coefficient of the acid higher than unity were obtainable in the presence of $Ca(NO_3)_2$. Which in terms of practical extraction of the acid means the possibility of extracting all the acid by the organic phase in a finite number of contact stages. Zharovskii and Melnik (108) extracted nitric acid with diethyl ether in the presence of different salting-out agents and these had different effects on the distribution coefficient. This was claimed to be because the degree to which water is bound to the salting-out agent varies with the electrostatic characteristic (radius and charge) of the cation of the salt.

The complete extraction of phosphoric acid by Baniel et al (109) as a purification process for wet-process acid, was based on the effect of salting-out agents increasing the distribution coefficient of the acid, especially at low acid concentrations where 'D' is normally very low when the acid is in its pure state. Since phosphate salts are not soluble in the aqueous phase in concentrations enough to provide a salting out effect, calcium chloride was used. In order to prevent the formation of calcium phosphates and free HCl (110), definite amounts of HCl were added to the system. The same principles are utilized in the processes for producing phosphoric acid by acidulating the phosphate rock with HCl (111 - 114) or HNO_3 (115 - 117) instead of H_2SO_4 as used in the conventional wet-process. In that case the salts formed from the reaction $CaCl_2$ or $Ca(NO_3)_2$ are soluble in the aqueous phase and have to be separated from the phosphoric acid by a liquid-liquid separation technique. However, the distribution coefficient of the acid for the nitrate-phosphate system is not high and most solvents do not give good separation (118). Commercialization of the process, therefore, has not yet taken place. On the other hand, processes based on the HCl acidulation of phosphate rock have been commercialized (IMI process (111)) and claimed to be successful (119). The salting out effect of calcium chloride on the extraction of H_3PO_4/HCl was justified by decreasing the water content in the solvent phase and the solvent content in the squeous phase (dehydrating effect), also by increasing the extraction of H_3PO_4/HCl into the organic phase.

2.3 PURIFICATION METHODS FOR WET-PROCESS PHOSPHORIC ACID BY ORGANIC SOLVENTS

Solvent extraction as a process for the purification of wet-process phosphoric acid is based on the ability of some organic solvents to extract the acid and reject, to a large extent, the impurities present. Therefore, there must be a difference of considerable magnitude in the distribution of acids and their simple salts between the solvent and aqueous phases.

Milligan (121 - 123) in 1932 was probably the first to attempt to use polar immiscible solvents for purifying wet-process acid. Later Cunningham (126) adapted the same principles with minor process modifications. They proposed the separation of the acid from calcium sulphate (gypsum) and other materials present in the sulphuric acid treated phosphate rock by dissolving it in organic solvent. An organic solvent was to be contacted with the liquor in a batch-wise or continuous extractor and the resulting extraction liquid separated by decantation, filtration or centrifugation. The acid could then be separated from the solvent by distillation, extraction into water, or by back extraction of the solvent into another organic solvent in which the acid would be insoluble, for example benzene or benzol. The organic solvent referred to by Milligan were mainly aliphatic monohydroxyl alcohols containing up to 8 carbon atoms, preferrably n-butyl alcohol. Ketones, aldehydes and esters were also claimed to be successful. Baniel and Blumberg (158) after examining Milligan's

approach found a number of serious limitations -

1. To dissolve phosphoric acid freely (completely) in a partially miscible solvent with water, its concentration should be higher than that corresponding to the plait point of the equilibrium diagram H_3PO_4-H_2O - Solvent (45% for n-butyl alcohol and 70% for iso-amyl alcohol). This obviously limits the amount of water that can be used in rock acidulation and would result in a very concentrated slurry that it is not practial to handle.

2. The reaction product had to be allowed to mature until the calcium sulphate hydrate became slow reacting, otherwise the solvent would reverse the reaction in which calcium phosphate is precipitated and sulphuric acid goes into solution. This would then be dissolved by the organic solvent.

3. Complete solvent recovery from the residual gypsum cake would be a rather costly process.

A similar approach was suggested by Keller (120) which involved the additon of an appreciably miscible and volatile oxygenated solvent to the acidulated phosphate rock liquor in a suitable contactor. The phosphoric acid would be leached into the water-miscible solvent phase and thus claimed to be substantially free from impurities. The solid residue containing gypsum and the rest of the impurities could be separated by filtration and the acid is regenerated by evaporating the

solvent. Subsequent purification of the acid by treatment with activated carbon was claimed to be possible. The organic solvents suggested by Keller were alcohols, ethers, ketones and esters soluble in water. Acetone was claimed to be particularly satisfactory. The use of completely miscible solvents in purifying wet-process phosphoric acid could suffer (158) from the limitations that solvents miscible with water normally have poor selectivity. Therefore, appreciable amounts of impurities are dissolved as well and extra costs are added to the production of acid when operating with relatively large amounts of a volatile solvent.

Because of the difficulties inolved in handling a gypsum-phosphoric acid slurry, most of the purification proposals are concerned with wet-acid after the separation of calcium sulphate. The acid thus produced is still far from pure and contains most of the acid soluble and suspended impurities from the rock and process reagents, e.g., Al, Fe, Ca, Mg, Si, F, SO_3 and other trace impurities. Typical compositions of some filtered and concentrated acids are given in Tables 2.2 and 2.3 respectively.

The purification methods described in Section 2.2 using partially immiscible solvents with water may be divided into two main processes: -

1. The direct extraction of the acid by contacting the impure acid at reasonably high P_2O_5 concentrations with a solvent in a multistage contactor. Because

the distribution of the acid with most suitable solvents is concentration dependent, it is usually only practicable to extract part of the acid as pure grade product leaving the remainder containing the impurities.

2. The second approach relies on the addition of either a salting out agent and/or a hydrogen ion source to increase the distribution coefficient of the acid at low acid concentrations; thus making it possible to extract all the available P_2O_5 as pure acid in a multi-stage contactor.

Another approach is based on the use of completely miscible solvents with water that are supposed to leach out the acid and enhance the precipitation of impurities.

All these approaches have been made the basis of processes to be described below, although they have not necessarily yet been commercialized.

2.3.1 Purification by Partial Extraction

The basic flowsheet for the partial extraction of phosphoric acid is presented in Figure 2.1. The extraction, purification and washing steps are mainly countercurrent single or multistage extractions; the raffinate stripping and acid concentration steps are mainly based on distillation and evaporation methods.

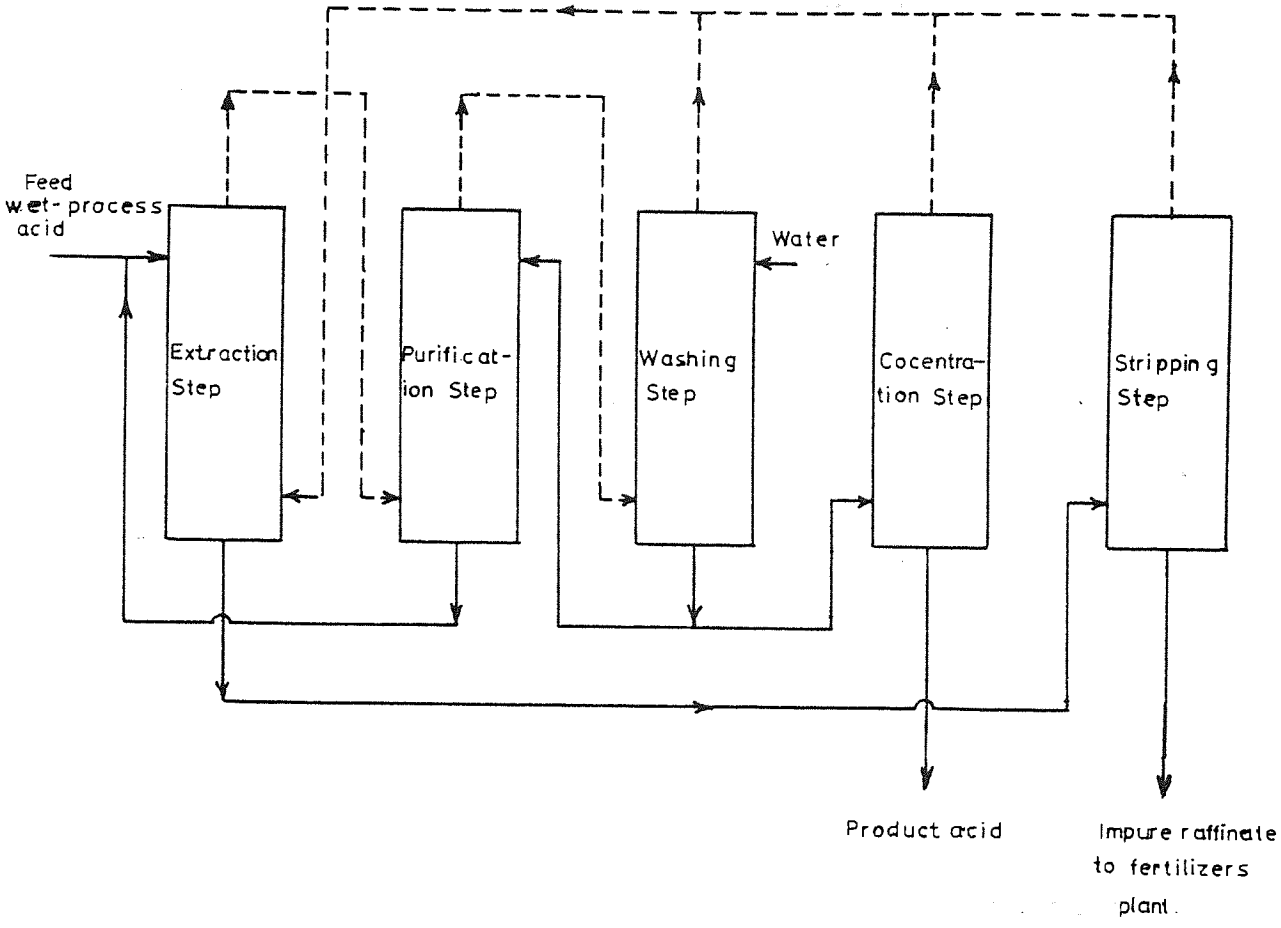


Fig.2.1 Basic flow-sheet for wet-process phosphoric acid purification by partial purification methods

– – – – Solvent phase

——— Aqueous phase

In all the processes described the pure acid leaving the extraction system is more dilute than the starting feed acid and its concentration, its relative quantity and quality are functions of the equilibria in the basic ternary system, and the selectivity of the solvent towards the acid and against the impurities (the separation factor) for each individual case. The solvents suitable for phosphoric acid extraction were divided (124) into two groups:

1. Solvents in a system in which the distribution coefficient of the acid is reasonably constant down to fairly low acid concentrations and only gradually changes with acid concentration as represented in Figure 2.2. Suitable solvents that may be classified in this group are mainly alcohols and alkyl phosphates, but amines are also included (124).

Vana (125) in 1934 was the first to attempt to purify wet-process acid, using oxygenated cycloparaffins such as cyclohexanol. A process based on aliphatic alcohols was described by the Toyo Soda Manufacturing Company (127) and in the preliminary economic estimate published by them, they claimed that it is possible to produce high purity acid at a cost below that provided by the thermal methods. The addition of minor amounts (5-20%) of a water insoluble monohydric alcohol to an alkyl amine was claimed (123, 129) to increase the extraction efficiency.

Alkyl phosphates, particularly tri-n-butyl phosphate, and also aryl phosphates have been claimed (130 - 133) for practical extraction purification processes. These patents are basically similar except in the way they treat the acid prior to its

extraction. Patents (130 - 131) suggest the addition of fluoride ions or boron compounds to prevent the formation and accumulation of gelatinous silica, while patent (132) suggests the addition of phosphate rock to increase the acid concentration; and sodium carbonate to precipitate residual sulphate and fluosilicate impurities as insoluble sodium fluousilicate. It was also suggested (132) that dilution of the solvent with another organic solvent having limited solubility in water such as benzene improved phase separation by lowering the viscosity and density of the organic phase.

Long chain alkylamines and/or amine salts dissolved in an organic diluent were claimed (133) to partially extract the phosphoric acid by forming complex anions. Another patent (134) proposes the reduction of Fe^{3+} to Fe^{2+} before extracting the acid with an amine extractant possibly to prevent the iron from being extracted with the acid.

2. Solvents that show very little extraction capacity for phosphoric acid below a specific threshold concentration. In other words, the distribution coefficient of the acid is very sharply concentration dependent as represented in Figure 2.3. This threshold concentration will place a limit on the residual impure acid concentration so the extraction is more limited than with solvents in group (1), since an increase in the number of stages will not increase the yield. Ethers, glycol ethers, esters and selected ketones were included (124) in this group and their threshold concentration

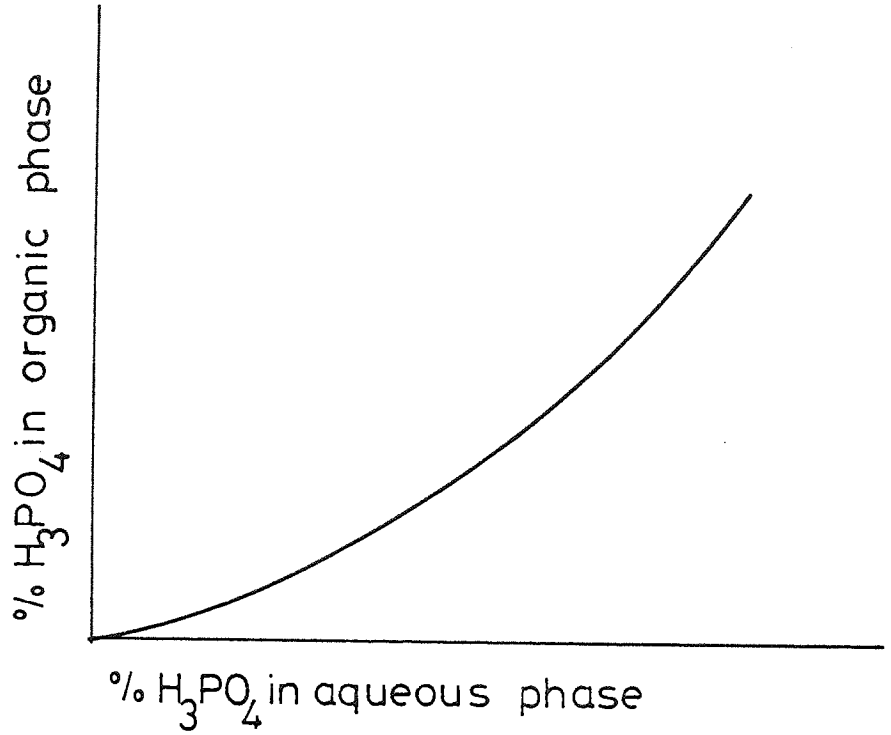


Fig. 2.2. Representative distribution curve for group(1) solvents

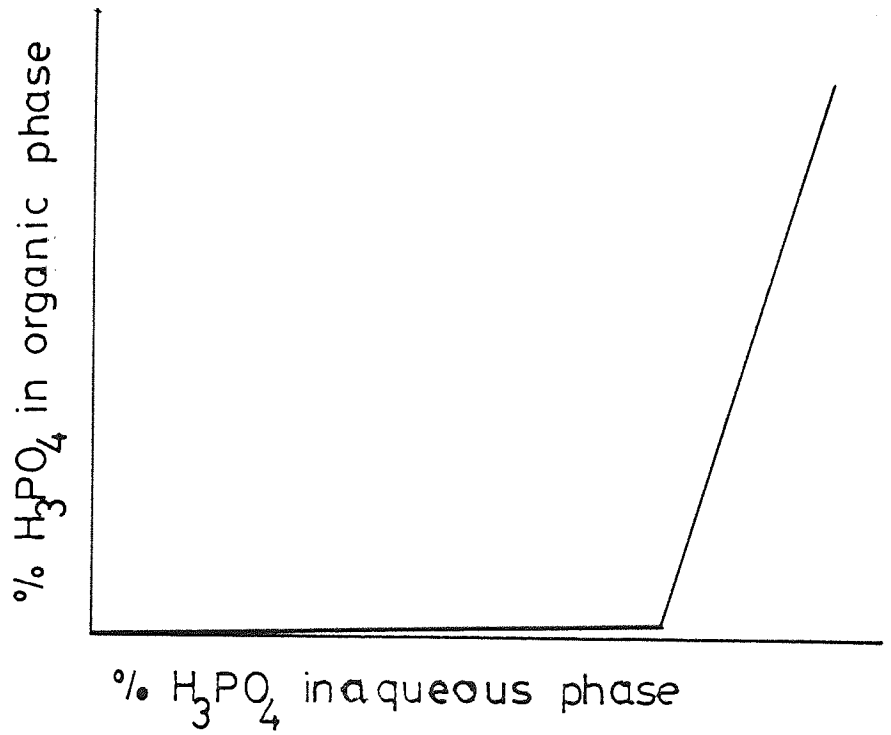


Fig. 2.3. Representative distribution curve for group(2) solvents

was found to be temperature dependent. Processes based on di-isopropyl ether and diethyl ether to extract concentrated acid were claimed by Schallert et al (89, 90). In these, complexes were formed and a three phase region was reported. The complex formed with di-isopropyl ether (IPE) was represented by the formula $H_3PO_4.H_2O.(CH_3)_2CHOCH(CH_3)_2$ (approximately 45% H_3PO_4, 8% H_2O and 47% IPE). With di-ethyl ether (EE) the complex was $H_3PO_4.H_2O\ (CH_3CH_2)_2O$. The three phase region was claimed to be formed because the complex is not appreciably soluble in either aqueous H_3PO_4 solutions of lower than a certain threshold concentration (68% H_3PO_4 with IPE and 53.8% H_3PO_4 with EE) or in excess solvent. The total amount of phosphoric acid complexed with the solvent was found to be linearly proportional to the acid concentration for aqueous solutions having H_3PO_4 concentration higher than the specific threshold value.

Several patents were claimed by IMI (97 - 102, 135) for partial purification of phosphoric acid using ethers such as di-isopropyl ether, di-n-butyl ether, di-n-amyl ether and diethyl ether; glycol ethers such as diethylene glycol; esters such as butyl acetate; and ketones such as cyclohexanone. The capacity of these solvents to extract the acid was found to be inverseley proportional to the operating temperature. Accordingly it was proposed to extract the acid from the aqueous phase in the extraction step at a low temperature (0 - 5^{o}C) and to release the acid from the extract in the washing step at a high temperature (40 - 60^{o}C) with or without

addition of water. By this treatment the purified portion of the acid could be recovered at relatively high acid concentration. Impure feed acid treatement to improve the product acid colour, or to combine and precipitate impurities was claimed (97) by applying various reagents to the acid prior to its extraction. The resulting precipitates were retained by the raffinate (impure portion).

The appearance of a limited third phase was also mentioned (101) when ethers were used, and the extent of this region was found to be affected by temperature changes. Baniel and Blumberg (158) described a process based on temperature cycling of the solvent and showed the effect of temperature change on the ternary system H_2O - H_3PO_4-di-n-butyl ether.

A process has been described (136) based on the use of esters selected from propyl acetates, butyl acetates, amyl acetates and mixtures thereof. However, esters were said (124) to hydrolyse in the system which is a factor of economic significance against their choice as solvents.

Albright and Wilson (137) claimed a process based on a solvent chosen from saturated acyclic ketones containing five or six carbon atoms. Of these, methyl isobutyl ketone (MIBK) was preferred (138) when extracting concentrated acid (70% H_3PO_4) because it has a high flash point and is therefore not unduly hazardous. If less concentrated acid is to be used as the feed (for example the 40-42% H_3PO_4, filter acid), a pentanone such as diethyl ketone or methyl-n-butyl ketone is

needed. These solvents have lower flash point and are more miscible with the aqueous phase than MIBK and, therefore, it is preferred to operate on concentrated acid using MIBK. A commercial plant for purifying wet-process phosphoric acid has been commissioned by Albright and Wilson at Whitehaven, Cumbria probably based on MIBK. Other plants for partially purifying the acid based on solvent extraction have been reported. The first was by Toyo Soda Manufacturing Company (1000 ton per month) installed in 1962 (139) probably operating on isoamyl alcohol. Since then other small scale plants have been constructed. In Japan (140), 3200 ton/month, by Nippon Kakagu Koguo; 1600 ton/month by Rasta; and 1500 ton/month by Rin Kagaku. In Mexico by FFM (141) a plant of 17500 tons/year licenced by IMI, based on di-isopropyl ether was under construction in 1971.

To understand the behaviour of different solvents for extracting any solute, a knowledge of the phase equilibrium of the system is vital. As mentioned earlier, the distribution of phosphoric acid between solvent and aqueous phase with most suitable solvents is concentration dependent. In some cases it is a gradual change (as in Group 1) in others it is a step change (as in Group 2). Moreover, the shape of the ternary diagrm and the relative size of the heterogeneous area may differ from one system to another. Therefore the whole extraction pattern will change. At a particular concentration one solvent may appear to be suitable, while at a different concentration, this same solvent may not be suitable, for instance because the phases become completely miscible. Alternatively the distrib-

ution coefficient may be very low or the mutual miscibility between the solvent and aqueous phases may be appreciable when selectivity of the solvent for the acid would decrease. In addition, the solvent must show preference for the acid against the impurities when dealing with impure acid, otherwise purification by solvent extraction cannot be fulfilled.

It has been the policy of industry to build up a patent structure around a central theme without revealing full information about it. Moreover, minor modifications may give the right to claim new patents, even though they are based on the same scientific principles.

Study of the phase equilibrium diagram for phosphoric acid-water-solvent was first reported by Ust-kachkinstev and Khlebnikov (142) in 1939 with diethyl ether as the solvent. The same system was later determined by Bachelet et al (143).

Seaton and Geankoplis (106) studied the effect of concentration and temperature on the distribution coefficient of HCl and H_3PO_4 and the effect of concentration on the mutual solubility of water and solvent for n-butanol, 2-hydroxyethyl n-hexyl ether and cyclohexanol. They also determined the distribution coefficient (D) of the two acids for many other solvents at one unspecified acid concentration, from which they concluded that alcohols were the best solvents for extracting both HCl and H_3PO_4 and that D_{HCl} was greater than $D_{H_3PO_4}$ for most solvents. However, the extraction capability of different solvents cannot be reached from one distribution coefficient value as mentioned

earlier.

The ternary phase diagram for H_3PO_4-water-solvent for many solvents was determined by several workers. The composition of the coexisting phases (tie lines) in the corresponding systemsand the distribution (partition) coefficients are given in appendix (II). A comparison between these systems is made in Table 2.4 with reference to Figure 2.4. The subscripts on the figure and the table have the following meaning:

a - solubility of solvent in water in the binary system.

b - solubility of water in solvent in the binary system

c - maximum point of the binodal curve.

d - critical isothermal solubility point (plait point).

From a study of the various phase diagrams the following conclusions can be reached:

1. The heterogeneous region within each group of solvents increases with increasing length of carbon chain of the solvent molecule, and therefore the mutual miscibility between the aqueous and solvent phases decreased accordingly.

2. The longer the solvent molecule chain, within each group, the higher should be the feed acid concentration to achieve practical extraction.

3. The higher the mutual miscibility, the greater will be the dilution effect. However, conversely the smaller will be the amount of solvent to be handled.

4. The maximum point of the binodal curve with most solvents is shifted towards the phosphoric acid-water binary system.

TABLE 2.4 : Comparison of Phosphoric Acid - Water - Solvent Systems

Solvent	Temp °C	a	b	c		d		Ref.
		Solvent Wt.%	Water Wt.%	Phos. acid Wt.%	Water Wt.%	Phos. acid Wt.%	Water Wt.%	
n-buty alcohol	25,35	7.5	20.0	42.7	50	35.5	37.7	147
iso bulyl alcohol	20,30	9.5	14.5	47.0	45.0	33.0	26.0	144
n-amyl alcohol	25	2.6	10.0	67.5	27.7	61.5	21.5	145
iso amyl alcohol	25,35	3.5	9.5	65.8	33.0	61.2	27.7	147
cyclohexanol	25	3.6	11.4	61.3	35	56.0	29.7	146
diethyl ether	23	6.53	1.24	48.5	40			143
dipropyl ether	25	0.17	0.24	81.4	14.0	53.1	5.8	148
di isopropyl ether	25	1.37	0.38	67	29	44	12	149
di butyl ether	25	0.18	0.66	90	8	57	4	149
di isoamyl ether	25	0.24	0.64	96.9	3.7	67	2	149
Methyl ethyl ketone	25	23.53	11.53	14.83	53	11	34	150
Cyclohexanone	25	8.63	5.47	31.9	50.8	27.4	38	150
Acetaphenone	25	0.71	1.37	crystal formation at high acid concn.				150
Methylhexyl ketone	25	0.19	1.12	79	18	69	18.1	151
di isobutyl ketone	25	0.19	1.41	90.38	7	48.4	4	151
Ethyl acetate	25	7.47	3.58	45.69	42	27.8	18.8	152
butyl acetate	25	0.76	1.46	72.48	26	48.5	13.8	152
amyl acetate	25	0.22	1.2	78.86	20	44.3	8.6	152
90% butanol + 10% Am (1)	25	11	23	4.8	60			153
90% butanol + 10% Am (2)	25	0.0	1.0	48	42	38	22	153
90% butanol + 10% Am (3)	25	10	19	48	42	41	25	153
60% butanol + 40% Am (4)	25	crystallisation of salt takes place						153
Benzaldehyde	25	0.33	0.30	77.1	20.8	58.18	12.17	154
Salicylaldehyde	25	0.58	0.98	78.5	16.6	40.7	5.65	154
furfural	25	8.18	5.09	37.0	45.0	26.9	26.8	155
m.cresol	20	3	2	96	2			156

(1) n-butyl amine

(2) tri-ethylamine

(3) Di-ethyl amine

(4) Di-ethyl amine

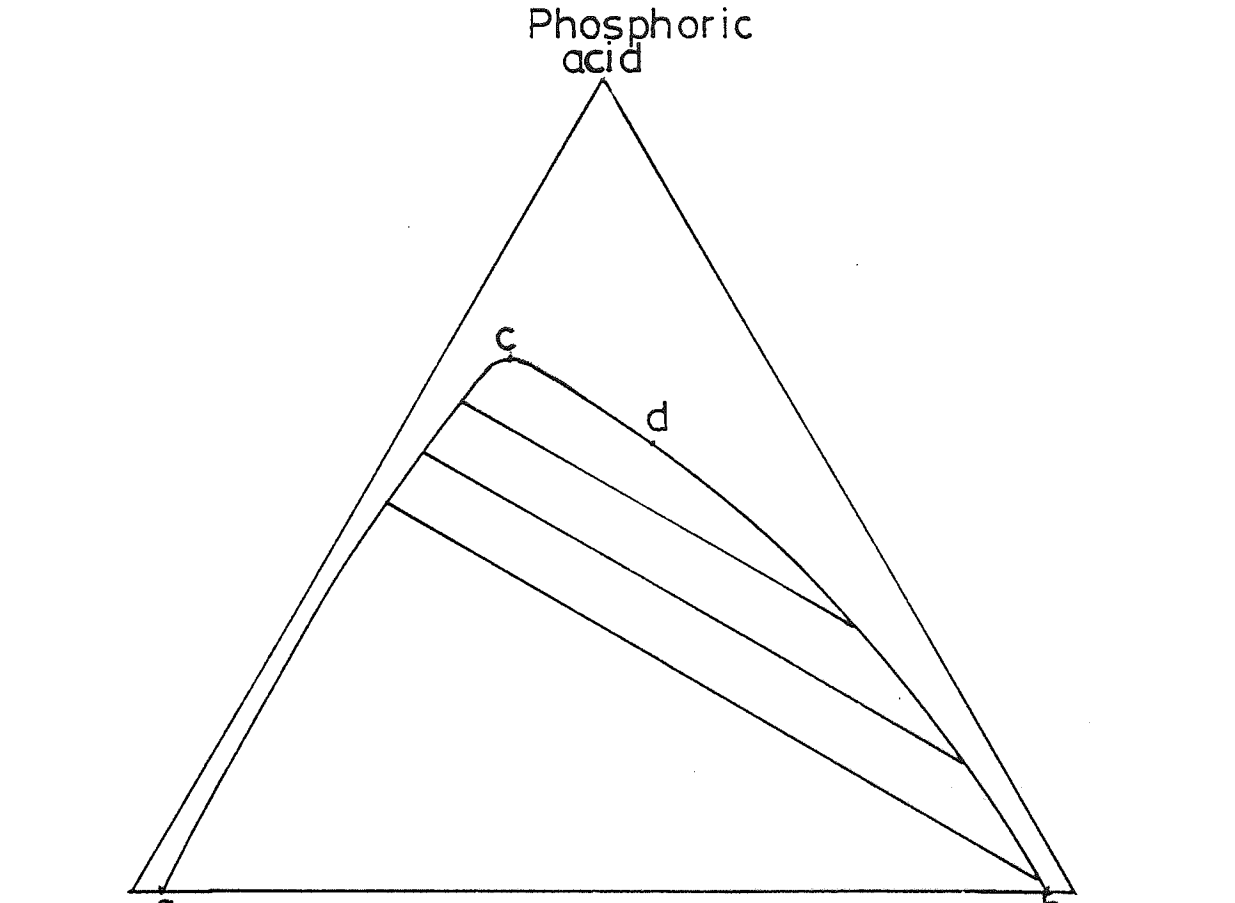


Fig. 2.4 Representative ternary phase equilibriam diagram for the systems Water - Phosphoric acid - Solvent

5. The binodal curve of some alcohol systems (147) is not affected much when the temperature changes from 25 to 35°C.

6. For those ethers studied it was concluded (149) that a solvent with a given number of carbon atoms is more effective for the extraction of acid if it has an iso rather than a normal structure.

7. For those ketones studied (151) it was found that straight chain aliphatic ketones with assymmetrical molecules such as methyl hexyl ketone are better than symmetrical ketones such as di-isobutyl ketone.

8. The presence of amine salts as a fourth component affects the system H_2O - H_3PO_4 n-butanol in different ways. When n-butylamine is present at 10% concentration the size of the heterogeneous area was reduced considerably and with the increase of amine content the heterogeneous region was further reduced. The presence of 10% triethyl amine, however, decreased the mutual miscibility (increased the heterogeneous region) between water and n butanol. The same effect, but to a lesser extent is demonstrated in the presence of 10% of diethylamine, and both amines were found to increase the distribution coefficient of the acid. When the diethyl amine content was increased to 40%, the whole binodal curve could not be investigated owing to crystallisation of the amine salt with increasing acid concentration.

Kim et al (157) studied the conditions affecting the purification of simulated wet-process phosphoric acid. Eight solvents were selected from a previously unpublished screening

study on 40 promising solvents as extractants of the acid. The effectiveness of these solvents (methyl ethyl ketone, 1-butanol, 1-heptanol, 2-methyl-1-propanol,1-pentanol, tert-pentanol, tri-n-butyl phosphate, di-isopropyl ether and isophorone) for separating impurities from simulated acids containing 35 - 75% H_3PO_4 was tested. Di-isopropyl ether was dropped from the test because it was claimed to be effective only with acids containing at least 75% H_3PO_4 , probably due to the formation of a three phase system at lower acid concentrations.

The first three listed solvents were found promising enough for more intensive tests which included the study of the effect of the concentration of impurities (Fe_2O_3, Al_2O_3, MgO, SO_3 and F), the partial neutralization of the acid with ammonia, and the initial concentration of the acid, all at room temperature. Although methyl ethyl ketone is completely miscible with aqueous phosphoric acid solutions at practically all acid concentrations and butanol mixes with aqueous acid solutions having higher than 50% H_3PO_4 (147,150), the experimental procedure laid down for extraction was the same as that for immiscible solvents. The results obtained were treated in the same way in terms of the proportion of acid extracted and the distribution coefficient. The most significant concluded effects were:

1. The higher the initial H_3PO_4 concentration, the better the extraction.
2. Increase of the anion impurity (SO_3 + F) increased the extraction of H_3PO_4 slightly, but also increased the

extraction of the metallic impurities.

3. Addition of ammonia increased the separation of the impurities (better quality extracted acid), but decreased the amount of H_3PO_4 extracted.

Although, no comments were made about the effect of metallic impurities, it can be concluded from the statistical constants reported that they probably have a negative effect on the acid extraction.

In general, partial purification methods have the following advantages (158):

1. Practical extraction usually necessitates operating with high acid concentrations. Although this is a limitation, it provides high throughput per unit equipment volume.
2. A small number of operations and no additional materials are needed.
3. Distillation or evaporation are only used for stripping solvents from aqueous streams and not for the main solvent recovery.
4. The product can be recovered with relatively little reduction in its concentration compared with the feed.

On the other hand, the method has some limitations:

1. Feed acid concentration should normally be high to make the process economically attractive, but the feasible concentration will depend on the solvent used.

2. The residual acid containing the feed impurities must be used in the production of solid phosphate fertilizers or in some other process where purity is not a critical property.
3. Some impurities such as SO_4 are only partially removed.

It seems generally agreed that the following results can be achieved from partial purification methods (158):

1. The fraction of purified acid may be increased up to approximately 90% of the feed, depending on the solvent, phase ratio and number of extraction stages.
2. Colour should be greatly improved.
3. Concentration of F^- can be greatly reduced and can be virtually removed by minor treatment of the feed.
4. Total cations, excluding H^+, can be reduced to 0.1 - 0.2%

The purified acid product should be suitable (158) for several products depending on the extent of purification e.g. Feed-grade phosphates, Liquid fertilizers, Sodium phosphates or as a reagent for organic reactions.

2.3.2 Purification by Complete Extraction of the Acid

As mentioned earlier, this could be achieved using two possible procedures (i) with solvents immiscible with the impure acid, using a salting out agent and/or a hydrogen ion source to boost the distribution coefficient of the acid at low H_3PO_4

concentrations; (ii) with completely miscible solvents, the acid being leached out and thus separated from the impurities.

2.3.2.1 Complete Extraction with Immiscible Solvents

These methods can be divided into two groups; the addition of a salting-out agent, and the addition of another acid, e.g. sulphuric acid.

A. Purification in the presence of salting-out agents, e.g. calcium chloride (109, 158) or calcium nitrate (159). These processes are based on the same principles and adapted from processes for preparing phosphoric acid by acidulation of phosphate rock with hydrochloric acid (110 - 114, 160 - 170) or nitric acid (115 - 117, 171, 172) instead of sulphuric acid. The basic flow sheet for a purification process (109) based on calcium chloride addition is shown in Figure 2.5. The concentration of calcium chloride needed to produce greatest extraction of the phosphoric acid depends on the acid concentration itself. When the initial acid concentration is low the Ca^{2+} content must be relatively high and vice versa. The effect of Ca^{2+} on the distribution coefficient of phosphoric acid at various H_3PO_4 and $CaCl_2$ concentrations is given in Table 2.5 (158).

To prevent the reaction of calcium chloride with phosphoric acid which results in the formation of calcium phosphate and free hydrochloric acid, HCl is usually added to the extraction system. It also serves to increase the distribution

coefficient of phosphoric acid (106, 110), as shown in Table 2.6 (110).

Hydrochloric acid after separation from the product acid is recycled in the process. However, if a source of HCl is available, it can be used to dissolve part of the phosphate rock and thus provide the necessary amount of $CaCl_2$ and some extra phosphoric acid. The resulting liquor is combined with an appropriate quantity of wet-process acid and the process flow-sheet can be represented by Figure 2.6. In this case the $CaCl_2$ and HCl are replenished in each cycle and the impurities are discarded together with the waste $CaCl_2$ brine. The $CaCl_2$ brine after extraction is treated to precipitate impurities and then reconcentrated to give the correct composition on mixing with wet-process acid.

Suitable organic solvents are those with which the acid shows reasonably constant distribution coefficient down to fairly low H_3PO_4 concentrations. Alcohols e.g, butanol or amyl alcohols; and trialkyl phosphates such as tri-n-butyl phosphate have been suggested.

Calcium chloride as a salting-out agent decreases the mutual miscibility between aqueous and organic phases and increases the distribution coefficient of the acid in the system as explained earlier.

The phosphoric acid, now substantially free from impurities together with part of the hydrochloric acid is extracted in a multiple countercurrent extractor. The calcium chloride,

the balance of the hydrochloric acid and the impurities remain in the aqueous raffinate. Hydrochloric acid is separated from the aqueous raffinate phase by a second solvent extraction operation, preferably using the same organic solvent. The extract phase is then washed with water in a countercurrent extractor to separate solvent from aqueous phosphoric and hydrochloric acids. These are then separated from each other and concentrated by distillation and evaporation. The product acid was claimed (158) to be of high quality satisfying detergent or food product specifications.

Clearly, the method has the advantage of extracting all the H_3PO_4 value. But the process is relatively complicated and can be rather costly if HCl and $CaCl_2$ cannot be cheaply provided. A plant based on this approach using isoamyl alcohol was constructed by IMI (161) in 1961. Another was constructed by Foret S.A. (Spain) and has been in operation since 1969 (140, 141), but the process details have not been disclosed.

B. Purification in the presence of a second acid. The addition of a second acid (generally concentrated H_2SO_4) to wet-process acid was claimed (99) to improve the distribution coefficient of H_3PO_4. Although sulphuric acid is also extracted by the solvent, its proportion is normally less than that in the feed. The basic flow-sheet is similar to those for partial purification and any suitable immiscible solvent may be used.

TABLE 2.5 : Influence of $CaCl_2$ on the extraction of H_3PO_4 in the system H_3PO_4-$CaCl_2$-H_2O-isoamyl alcohol (109, 158)

H_3PO_4 gm/lit	Composition, wt %		Distribution Coefficient
	H_3PO_4	$CaCl_2$	
135	11.5	18.5	0.50
135	11.5	4.2	0.15
135	11.5	0	0.07
165	13.5	16.0	0.32
165	13.5	6.0	0.14
176	14.5	19.0	0.50
176	14.5	12.0	0.42
176	14.5	6.0	0.20
200	16.5	19.3	0.40
200	16.5	16.6	0.32
235	19.0	3.1	0.33
250	20.0	16.6	0.32
250	20.0	3.1	0.33
250	20.0	0	0.13
475	34.9	4.6	0.23
475	34.9	0	0.21
740	48.9	9.7	0.37
740	48.9	0	0.41
1060	62.9	2.2	0.48
1060	62.9	0	0.68

TABLE 2.6 : Influence of HCl on the extraction of H_3PO_4, HCl and $CaCl_2$ with n-butyl alcohol and isoamyl alcohol at 1:1 volume ratio of the phases at 25°C (110)

Exp. No.	HCl concen. in the initial alcohol wt.%	Aqueous Phase				Organic Phase				Distribution Coefficient	
		Specific gravity gm/cm³	Equilibrium concentration wt.%			Specific gravity gm/cm³	Equilibrium concentration wt.%			D	D
			P_2O_5	HCl	$CaCl_2$		P_2O_5	HCl	$CaCl_2$	H_3PO_4	$CaCl_2$
1	0	1.3624	7.11	0.076	27.2	0.8876	5.05	3.41	0.78	0.71	0.027
2	3.06	1.3193	6.25	1.30	26.9	0.8949	5.04	4.77	0.45	0.81	0.017
3	6.02	1.3090	5.76	2.99	26.4	0.9051	5.28	5.70	0.52	0.92	0.020
4	12.0	1.2892	5.80	5.64	23.5	0.9057	5.42	7.78	0.57	0.93	0.024
5	0	1.3437	6.21	0	29.5	0.9197	6.36	3.67	2.05	1.17	0.07
6	2.0	1.3182	5.07	0.39	28.8	0.9271	6.49	4.24	1.33	1.28	0.05
7	4.0	1.3153	5.01	1.31	28.0	0.9281	6.46	5.37	1.45	1.29	0.05
8	6.0	1.3121	5.04	1.98	26.2	0.9354	6.49	6.24	1.13	1.29	0.043
9	8.0	1.3157	5.03	2.80	25.7	0.9795	6.44	7.60	1.15	1.28	0.045

Remarks:

1) Experiments 1 - 4 are with iso amyl alcohol and 5 - 9 are with n-butyl alcohol.

2) In all experiments except No. 5, the initial aqueous acid composition is 9.71% P_2O_5, 2.63% HCl and 24.3% $CaCl_2$. In experiment No. 5, the initial aqueous acid composition is 9.97% P_2O_5, 2.99% HCl, and 25.3% $CaCl_2$.

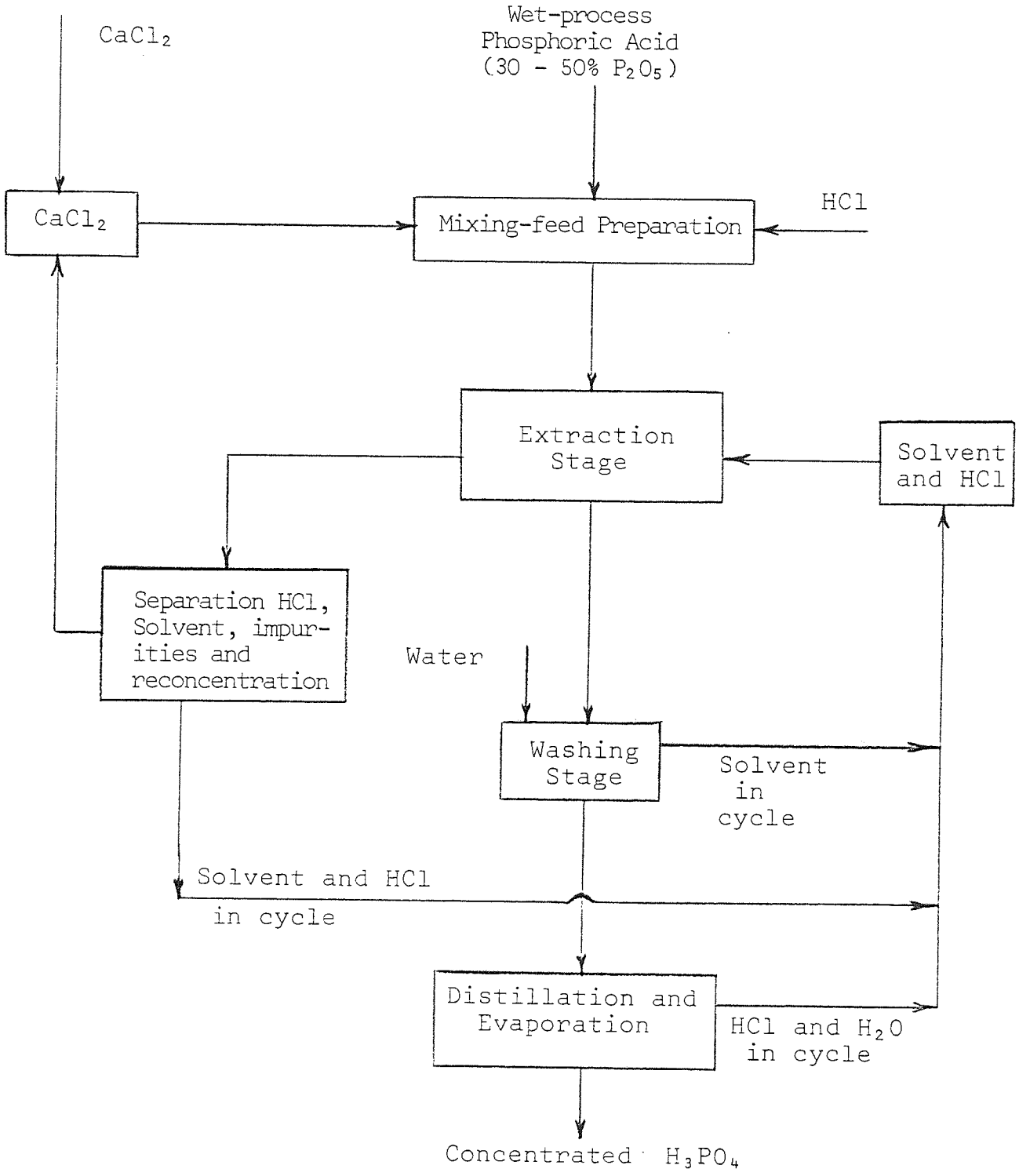


FIGURE 2.5 : Purification of wet-process phosphoric acid with $CaCl_2$ in cycle

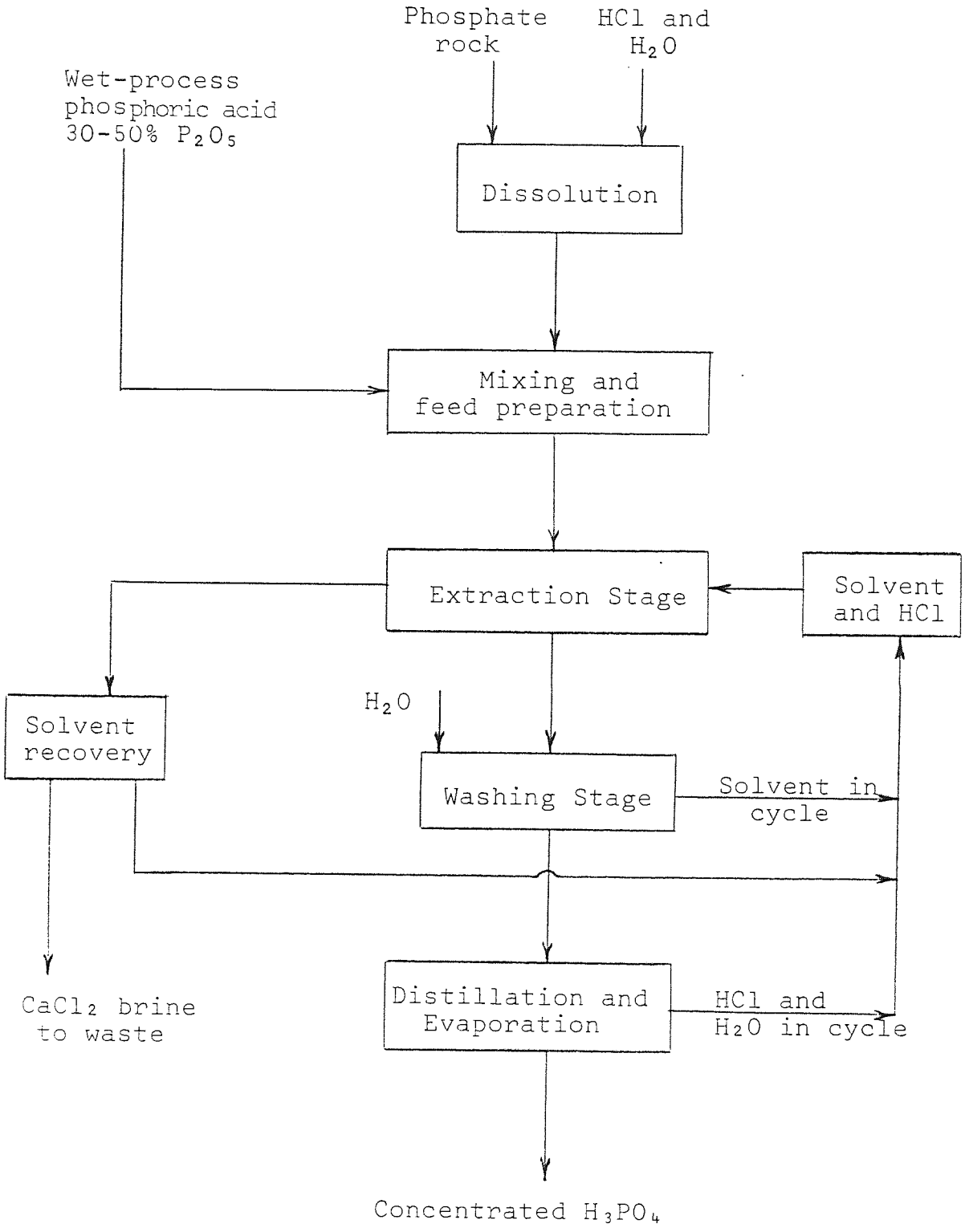


FIGURE 2.6 : Purification of wet-process phosphoric acid with external source of HCl.

This approach has been recommended for extracting phosphoric acid from aqueous raffinate solutions resulting from partial purification methods. Concentrated sulphuric acid in an amount from 30 - 100% by weight of the phosphoric acid is added to the aqueous raffinate and the resulting mixture is re-extracted, preferably with the same solvent employed in the primary extraction stage. The acids can be either neutralized with ammonia and thus precipitated for direct use in fertilizers or extracted back into water and used for phosphate rock acidulation. Although most of the H_3PO_4 value may be recovered, the method suffers because the final aqueous phase is rich in sulphuric acid together with impurities. This might not find an end-use and, therefore, extra cost could be incurred for waste disposal. The other limitation is that the recovered phosphoric acid is mixed with a large amount of sulphuric acid, for which separation is costly if pure H_3PO_4 is required.

2.3.2.2 Complete Extraction with Miscible Solvents

This method involves mixing wet-process phosphoric acid with a completely miscible organic solvent, where the acid is leached out and precipitation of impurities is promoted. The precipitates could be separated by filtration and the solvent by distillation, before it is recycled to the process.

Alcohols, preferably a mixture of 1:3 methanol to isopropanol was claimed (173) to result in better purification

of the acid than that achieved with either alcohol individually. Other organic solvents such as ethanol, methyl ethyl ketone and acetone were also claimed to be successful, especially when applied in conjunction with the addition of ammonia (174, 157), an ammonium salt or an alkali metal salt (175, 176) prior to the addition of solvent. The addition of these compounds was claimed to produce better quality acid but it also decreases the amount of recovered H_3PO_4 value.

This approach has other limitations. The product although of improved quality, is still far from pure and contains a considerable amount of impurities. Subsequent purification using a strongly acid cation exchanger was suggested (175). Large amounts of material are used, 200 - 500% of solvent and 10 - 20% of ammonia per weight of acid. The solvent must be recovered by distillation while the ammonia can be difficult to recover economically. The recovery of solvent from the filter cake can also be expensive.

2.4 SOLVENT SELECTION

The strategy of this work was as follows: -

1. In order to select a solvent, it is first necessary to study and understand in general the extraction of mineral acids with organic solvents and in particular solvent extraction for the purification of wet-process phosphoric acid.

2. Since the use of ammonia or other agents leads to a complicated and potentially expensive process, it was decided to

reject completely miscible solvents and concentrate on those where the difference in distribution coefficients of phosphoric acid and its salts between organic and aqueous phases could be exploited.

3. To assess the performance of any purification system, information about the ternary diagram, the effect of impurities, the hydrodynamic behaviour and other factors affecting the solvent choice are needed. To select the best solvent, suitable solvents should be examined and compared with each other.

4. Should one solvent appear to be particularly suitable, factors that improve its performance such as operating at different temperatures, the addition of a salting-out agent and/or a hydrogen ion source, should improve its performance even further. These conditions may generally be expected to affect most suitable solvents in a similar way.

5. It was, therefore, decided to study partial purification of the acid at one particular temperature (25^{o}C).

The solvents selected for extensive examination were n-amyl alcohol, tri-n-butyl phosphate, di-isopropyl ether and methyl isobutyl ketone. These solvents were chosen:

(i) To cover both main physical types of solvents. With the first two solvents the distribution coefficient shows a gradual increase, while with the last two solvents it shows a sharp increase with an increase in acid concentration.

(ii) To cover most suitable chemical types of solvents, i.e. alcohols, alkyl phosphates, ethers and ketones (see Section 2.2). The solvents selected represent almost the optimum choice within each type, in terms of distribution coefficients and mutual miscibility for the extraction of H_3PO_4 from concentrated wet-process acid (30 - 55% P_2O_5).

(iii) To use reported valuable solvents, these solvents have been extensively claimed in the patent and paper literature to be reasonably successful for the purification process.

Phase equilibrium information was only known to exist about pure H_3PO_4/water with n-amyl alcohol (145) and di-isopropyl ether (149). No information regarding the quantitative effect of impurities on the ternary phase diagrams or the hydrodynamic behaviour of any of the purification systems was available. Regardless of the published information, all the systems were evaluated in this study and distinct differences were noticed from those already published. These will be discussed later in Chapters 7 and 9.

The following factors must generally be considered in the choice of a suitable solvent:

1- Solvent Selectivity : In a ternary system the selectivity β of solvent (B) for solute (C) is defined as the ratio of concentration of solute (C) to nonconsolute (A) in the solvent-rich phase divided by the ratio in the aqueous rich phase:

$$\beta_{C,A} = \frac{X_{CB}}{X_{AB}} \cdot \frac{X_{AA}}{X_{CA}} \qquad (2.2)$$

In most cases, β vary widely with concentration. Practical extraction processes require that β exceeds unity, the more so the better. Rearranging equation (2.2)

$$\beta_{C,A} = \frac{X_{CB}}{X_{CA}} \cdot \frac{X_{AA}}{X_{AB}} = D_C \frac{X_{AA}}{X_{AB}}$$

Systems with an unfavourable distribution coefficient ($D < 1$), will not necessarily give values of β less than unity except if the mutual solubility of A and B is considerable.

In a quaternary system, where C and D are distributed between immiscible solvents A and B, the selectivity and distribution coefficients are related in the following manner:

$$D_C = \frac{X_{CB}}{X_{CA}} \qquad D_D = \frac{X_{DB}}{X_{DA}}$$

$$\beta_{C,D} = \frac{D_C}{D_D} = \frac{X_{CB}\ X_{DA}}{X_{CA}\ X_{DB}}$$

Again β must exceed unity for a successful process.

2. Distribution Coefficient : High values of distribution coefficients are desirable since it affects the selectivity and the number of contact stages required.

3. Capacity : Large solvent capacities to dissolve the preferentially extracted solute are required to minimize the amount of circulated solvent. High values of X_{CB} are therefore required in addition to high values of distribution coefficient.

4. Solvent Solubility : A high degree of insolubility of solvent B with the nonconsulte (A) is required to improve selectivity and minimize the recovery costs of solvent and product.

5. Recoverability : This has a major economical significance on the extraction process, since the solvent has to be re-used and product freed from contamination. With the systems envisaged in this work, solvent recovery is to be carried out by back extraction of the acid into pure water. The acid product and impure raffinate may have to be distilled or evaporated to remove the small percentages of solvent.

6. Density : The greater the density difference between the contacted phases the better to enhance settling of the phases. This results in better use of the equipment capcity.

7. Interfacial Tension : The larger the interfacial tension the faster will the coalescence of the emulsion take place. However, large interfacial tension makes the dispersion of one phase into the other more difficult. Coalescence is usually more important, and interfacial tension should therefore be high.

8. Chemical Reactivity and Stability : The solvent should be chemically stable and free from undesirable chemical reactions with the solute, the other solvent and materials of construction.

9. Viscosity, Vapour Pressure and Freezing Point : These should be low for ease of handling and storage.

10. Other Properties : The solvent should be nontoxic, non-flammable, and available at low cost.

CHAPTER THREE

MASS TRANSFER FUNDAMENTALS

In liquid-liquid extraction processes, the solution containing the solute is contacted with an immiscible solvent. The solute is transferred across the interface separating the lquids and this process continues until equilibrium has been established, when the chemical potential of the solute is the same in both phases. However the concentration of the solute in each phase will not be the same. Mass transfer occurs when the phases are not in equilibrium and the rate of transfer then depends on the physical properties of the phases, the hydrodynamics of the system and the relative solubility, or distribution coefficient of the solute in each of the phases. The rate of mass transfer can be described by an equation of the form

$$N_A = K.A.\Delta C \qquad (3.1)$$

where N_A is the mass transfer rate

K is the overall mass transfer coefficient

A is the interfacial area

and ΔC is the concentration driving force.

It is generally assumed that mass transfer in liquid-liquid systems consists of three relatively simple steps;

diffusion of the solute from the bulk of the raffinate phase to the interface, passage across the interface and diffusion into the bulk of the extracting solvent. Therefore, calculation of mass transfer rate in any liquid extraction process requires the knowledge of the resistance to transfer in each phase, the interfacial area and the driving force, as expressed in equation (3.1).

3.1 MASS-TRANSFER COEFFICIENTS

The mass transfer coefficient K embodies the characteristics of the laminar and turbulent flow regions of each phase and the molecular and eddy diffusivities in whatever proportions they may occur. It embraces three fundamental resistances, which are the dispersed and continuous phase film coefficients k_d and k_c and the interfacial resistance. The latter is usually very small and may be neglected. Therefore,

$$\frac{1}{K_d} = \frac{1}{k_d} + \frac{1}{mk_c} \quad \text{or} \quad \frac{1}{K_c} = \frac{1}{k_c} + \frac{m}{k_d} \qquad (3.2)$$

where m is the distribution coefficient of the solute. The choice of K_d or K_c depends on the driving force chosen in equation (3.1).

Mass transfer of a solute between a dispersed phase and a continuous phase can be imagined as a transfer between drops and the surrounding liquid and to understand the mechanism of mass transfer, a number of investigations of solute transfer

to and from single drops has been made (1 - 8). The models derived from such investigations describe the experimental results with a fair degree of accuracy, but their main weakness is that they are derived for single drops. When large numbers of drops are present, there may be considerable coalascence and break-up producing new surface area with associated mixing and surface renewal effects. These interactions affect the rate of mass transfer. Nevertheless, it is necessary to study mass transfer to and from single drops to gain information about the practical situation.

Mass transfer between a single drop and surrounding fluid is usually divided into three parts:

(i) Mass transfer inside the droplet.

(ii) Mass transfer through the interface.

(iii) Mass transfer outside the droplet through the surrounding fluid.

3.1.1 Mass Transfer Inside the Droplet

In the life of each drop there must be three distinct stages (1), and the mechanism of solute transfer is different in each stage. The stages are:

(I) Drop formation - at the nozzle or spray tip

(II) Drop movement - through the continuous phase.

(III) Drop coalescence - at the interface.

Stages I and III are termed end effects. Although neglected sometimes in practical extraction, they may have considerable effect on the solute transfer process (9, 10).

3.1.1.1 Mass Transfer During Drop Formation

The conditions under which solute transfer is occurring during the formation of a single drop from a submerged nozzle in a stationary solvent phase are probably as follows (4): While the drop is in the process of being formed, its interior must be in motion and of relatively uniform concentration. The surrounding continuous phase undergoes a small amount of viscous displacement due to the expansion of the drop. Hence, there is no film in the continuous phase surrounding the drop or rather, a "film" of infinite extent surrounds the drop.

Mass transfer during drop formation was investigated by several workers (1, 2, 9, 10) and was found to account for from 10% to 50% of the total solute transferred. It has a more significant effect in extraction columns than in agitated tanks. The mathematical analysis of this mechanism is given in references (4, 11).

3.1.1.2 Mass Transfer During Passage Through the Continuous Phase

The resistance to transfer to and from a drop depends upon the motion of the liquid inside the drop, whether it is stagnant (behaving as a rigid sphere), circulating or whether the drop

itself is oscillating. It has been reported that oscillation occurs in regimes of flow for which the droplet Reynold's numbers are larger than 200, below this circulation predominates (12). As would be expected, the greater the internal turbulance, the greater the K_d value.

Newman (13) developed an expression for the prediction of transfer rates in rigid spheres:

$$E = \frac{C_o - C_f}{C_o - C^*} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left[-n^2 \pi \frac{D_D t}{a^2}\right] \qquad (3.3)$$

From which

$$K_d = -\frac{d}{6t} \ln \frac{6}{\pi^2} \sum_{n=1}^{\infty} \left\{ \frac{1}{n^2} \exp\left(-\frac{4\pi^2 n^2 D_D t}{d^2}\right)\right\} \qquad (3.4)$$

Where the symbols have their usual meanings as given in the nomenclature.

When resistance to transfer in the continuous phase is zero and under a laminar circulation regime which can be described by Hadamard (14) streamlines, the expression of Kronig and Brink (15) can be applied:

$$E = 1 - \frac{3}{8} \sum_{n=1}^{\infty} A_n^2 \exp\left[-\lambda n \frac{16 D_D t}{a^2}\right] \qquad (3.5)$$

From which the mass transfer coefficient

$$K_d = -\frac{d}{6t} \ln \frac{3}{8} \sum_{n=1}^{\infty} A_n^2 \exp\left[\frac{-64\lambda n D_D t}{d^2}\right] \qquad (3.6)$$

Rose and Kintner (16) reported that droplet oscillation causes interfacial stretch which is accompanied by a variation in the driving force. This results in a very large increase in the rate of mass transfer. They developed a correllation for the mass transfer coefficient for an oscillating drop as follows:

$$K_d = 0.45(D_D w)^{\frac{1}{2}} \qquad (3.7)$$

where

$$w = \left(\frac{\sigma b}{r^2}\right)\left(\frac{1}{3\rho_d + 2\rho_c}\right) \qquad (3.8)$$

and

$$b = 0.805\ d^{0.225}$$

3.1.2 Resistance to Mass Transfer at the Interface

As mentioned above, the resistance to mass transfer across the interface must be negligible according to the Whitman theory (17) which postulates that interfacial equilibrium and resistance additivity are valid (equation 3.2)). However, there are conditions under which equation (3.2) does not appear to apply since the observed overall resistance (1/K) is either considerably larger or smaller than the one

estimated from the expected individual transfer coefficients. Some of these conditions might have a considerable effect on the interface mass transfer. They can be caused by physical or by chemical barriers. Temperature changes at the interface due to different heats of solution of the solute in the two liquids can change the physical properties (e.g. viscosity, density) that affect the individual mass transfer coefficients (17). Adsorbed trace substances (film impurities, dirt or surface active agents) can enhance interfacial resistance because of their influence in blocking the surface, reducing the mobility of the interface, inhibiting internal circulation, and possible interaction with the extracted solute.

Alternatively mass transfer at the interface may be enhanced by the Marangoni effect (18) which is produced by gradients in interfacial tension resulting from concentration gradients along the surface. The effect can be manifested in many ways, local disruptions, random disturbances and violent internal circulation (19). These may range in intensity from a negligible to a considerable effect on the individual transfer coefficient. Strictly, these are not interfacial resistances but effects that modify the coefficients. Accordingly these coefficients should be corrected at the postulation of equilibrium at the interface retained.

3.1.3 Mass Transfer in the Continuous Phase

Although the various stages in drop life and the factors affecting them have been recognised, the same is not true for

the continuous phase (20). Transfer from the bulk of the continuous phase takes place across a laminar film moving over the drop surface. It will differ according to the motion inside the drop. The continuous phase is usually assumed to be well mixed at the bulk concentration and temperature.

Linton and Sutherland (21) proposed the following correlation for the continuous phase coefficient for the case of rigid drops:

$$Sh = 0.582(Re)^{\frac{1}{2}}.(Sc)^{\frac{1}{3}} \qquad (3.9)$$

Heertjes and deNie (22) recommended the following correlation for circulating drops:

$$Sh = 1.13(Re)^{\frac{1}{2}}(Sc)^{\frac{1}{2}} \qquad (3.10)$$

Internal circulation lowers the thickness of the boundary layer around the drop, thus enhancing transfer rates. Garner and Tayban (23) suggested the following relation for oscillating drops:

$$Sh = 50 + 0.0085(Re)(Sc)^{0.7} \qquad (3.11)$$

3.2 INTERFACIAL AREA AND DROPLET PHENOMENA

Interfacial area is the available area for the solute to pass through from the raffinate to the extract phase. It

depends on many factors affecting the physical properties of the system and the mixing conditions. Large interfacial areas can be obtained in agitated liquid-liquid contactors (30 to 800 cm^2/cm^3) compared with those obtained in extraction columns (1 to 10 cm^2/cm^3) (24).

3.2.1 Estimation of Interfacial Area

The interfacial area has been estimated by different experimental techniques, these are listed below with the appropriate reference numbers.

1. Light transmittance (25, 26, 27)
2. Light scattering (28)
3. Photography (29)
4. Electronic particle counting (30)
5. Sedimentometry (31)
6. Liquid-liquid extraction by fast pseudo first order reaction (24).

The interfacial area can be calculated from a knowledge of average drop diameter (d_{32}) and dispersed phase ratio ϕ_d as follows:

$$A = \frac{6\phi_d}{d_{32}} \qquad (3.12)$$

where

$$d_{32} = \frac{\Sigma N_i . d_i^3}{\Sigma N_i . d_i^2}$$

3.2.2 Prediction of Drop Size

Droplet size in a turbulent flow regime is governed by two processes, droplet break-up due to shear through turbulence in the bulk flow and coalescence due to interaction forces which involve the combination of two or more drops to form a bigger drop.

With regard to droplet breakup, Hinze (32) identified various flow patterns and forces causing droplet deformation which in some cases cause droplet breakup. The controlling forces for droplet breakup are:

(a) The dynamic pressure τ

(b) The viscous stress $[\frac{\mu_d}{d} (\frac{\tau}{\rho_d})^{\frac{1}{2}}]$

(c) The surface tension force $\frac{\sigma}{d}$.

The first two forces cause deformation and the third resists deformation. From these three forces two independent dimensionless groups were selected

$$\text{Webber number} \qquad N_{we} = \frac{\tau d}{\sigma}$$

and

$$\text{Viscosity number} \qquad N_{vi} = \frac{\mu_d}{(\rho_d \sigma d)^{\frac{1}{2}}}$$

The greater the value of N_{we} the greater the deformation, and at a critical value, $(N_{we})_{crit.}$, breakup occurs.

Kolmogoroff (33) postulated that in turbulent flow a whole range of eddies exist. The large primary eddies are unstable

and disintegrate into smaller and smaller eddies until their energy is dissipated by viscous flow. The smaller eddies are pressumed to be independent of the bulk motion at high values of impeller Reynolds number. The characteristic properties of these eddies should, therefore, be determined by the local energy dissipation rate per unit mass 'ε'. The characteristic Kolmogoroff length is predicted by

$$\eta = \left(\frac{\nu^3}{\varepsilon}\right)^{\frac{1}{4}} \qquad (3.13)$$

where ν is the kinematic viscosity.

When $\eta << d$, breakup is mainly caused by the dynamic turbulent pressure fluctuations. Under this condition, Hinze (32) related the maximum stable drop size by

$$d_{max} = k_1 E^{-0.4}\left(\frac{\rho c}{\sigma}\right)^{-0.6} \qquad (3.14)$$

where

$$E = \frac{4k_2}{\pi} \cdot \frac{N^3 D^5}{H D_T^2}$$

Shinner and Church (34), using the Kolmogoroff theory, developed predictions for average drop size. For breakup as the predominant mechanism (low values of ϕ) they obtained:

$$\frac{d_{32}}{D} = k_3 N_{we}^{-0.6} \qquad (3.15)$$

For coalascence as an important process, they obtained

$$\frac{d_{32}}{D} = k_4 N_{we}^{-0.375} \left(\frac{A(h)}{\sigma D}\right)^{0.375} \qquad (3.16)$$

Where A(h) is to be thought of as an energy of adhesion between two drops of unit diameter separated by a distance h. Many other workers (25, 27, 35, 36) produced correlations similar to equation (3.15). Some of them accounted for coalescence by including the dispersed phase hold up. Sprow (37), by using the Shwarz-Bezemer equation related the average drop diameter d_{32} as

$$d_{32} = 0.38 d_{max} \qquad (3.17)$$

When $\eta \gg d$, break up is mainly caused by viscous stresses. For this case, based on Kolmogoroff theory, Shinner and Church developed the relation

$$\frac{d_{max}}{D} = k_5 \sigma \nu_c^{\frac{1}{2}} \mu_c^{-1} N^{-3/2} D^{-2} f(\mu_d/\mu_c) \qquad (3.18)$$

All these relations have been applied for non-mass transfer conditions. Caution is needed in using them since they do not generally agree with each other because of the different systems and equipment used.

3.3 DRIVING FORCE

The driving force in an extraction process can be described as the distance the system is away from equilibrium. The difference between the actual concentration of the solute in one phase and the concentration which should be in equilibrium with that in the other phase is the force tending to dissolve (or release from solution) the solute. It is the algebraic sum of these differences in concentration that cause the process to proceed.

Some investigators (38, 39, 40) sugested the use of chemical activities rather than concentrations, since the former are the same in both phases at equilibrium. However, the accurate measurement of activities is difficult in extraction equipments, and therefore concentrations are usually used to estimate the driving force.

Olander and Reddy (41) noticed that at very large driving forces, the transfer resistance is not independent of the concentration level and the direction and magnitude of the driving force. This was explained by the effects of property variations and interfacial velocity on mass transfer coefficient. These effects, generally termed interfacial turbulance, result from hydrodynamic instability at or near the interface caused by an interface concentration gradient. The over-all mass transfer coefficient for three systems studied increased sharply by factors of 1.5 - 4 as the driving force was increased. Licht and Conway (1) reported that, for equal driving force, the mass

transfer rate of acetic acid in an organic solvent - water system depends on the direction of mass transfer. This phenomenon is presumed to be the result of hydrogen bonding forces being stronger when acetic acid is extracted from water than when it is being extracted from the organic phase. Overcashier et al (42) found that the average mass transfer driving force itself was reduced by baffling in the mixer due to increased axial flow.

CHAPTER FOUR

LIQUID EXTRACTION EQUIPMENTS

4.1 EQUIPMENT CLASSIFICATION

Extraction equipment can be classified into two main categories:

(i) Stage wise (discrete stage) contactors

(ii) Continuous (differential) contactors

Each of these can be further subdivided depending on the type of agitation employed. Hanson (20) has given a typical classification for the most common units. A modified form of which is reproduced in Table 4.1.

4.2 EQUIPMENT SELECTION

4.2.1 General Considerations

The advantages and disadvantages of the two basic types of contactors are summarised in Table 4.2, but the choice of an extractor for a particular application depends mainly upon experience. However, careful analysis should be made for the design and process parameters before making the final choice, and some of these are discussed here.

TABLE 4.1 : Liquid-Liquid Extraction Equipment Classification

Type of Agitation	Stage Wise Contactors	Continuous Contactors
None		i) Spray Column (17, 46) ii) Simple Packed Column (17) iii) Wetted-wall Towers (17) iv) Baffle Plate Column (17)
Rotary device	i) Simple Mixer-Settler (17) ii) Pump-mix Mixer-Settler (43) iii) Stacked-stage Mixer-Settler (46)	i) Rotating Disc Contactor (17,46) ii) Sheibel Column (44) iii) Old Shue-Rushton Column (45) iv) Luwesta (46)
Centrifugal device	i) Robatel Mixer-Settler (20)	i) Podbiel niak Extractor (46)
Pulsing device	i) Pulsed Mixer-Settler (46)	i) Pulsed packed Column (17,46) ii) Pulsed sieve-tray column (17,46)

TABLE 4.2 : Advantages and Disadvantages of the Two Basic Types of Contactors

Continuous Differential Contactors	Discrete Stage Contactors
ADVANTAGES	
1. Low initial cost	1. Good contacting
2. Low operating cost	2. Handles wide flow ratio
3. Simple in construction	3. High efficiency
	4. Handles large number of stages
	5. Low headroom
	6. Reliable scale up
	7. Flexibility in operation
DISADVANTAGES	
1. Small density difference	1. Large hold up
2. Limited through put	2. High power cost
3. Cannot handle wide flow ratio	3. Large floor space
4. Sometimes low efficiency	4. High investment
5. High headroom	5. Interstage pumping may be required
6. Difficult to scale up due to back mixing effects.	

(i) The number of effective contact stages required. All types of extractors can be used satisfactorily when few stages are needed. For economy column extractors are preferred for processes involving a large number of stages. However, mixer-settlers may have to be used for processes requiring more than twenty stages because of practical limitations.

(ii) Throughput. From the economic point of view, spray towers or packed columns could be used for low throughputs, while RDC's, pulsed plate columns or mixer-settlers could be used for intermediate and high throughputs.

(iii) Solvent residence time. This is especially important when handling materials of low stability. Centrifugal extractors are normally preferable since they can provide fast settling rates if the interfacial tension of the system processed is suitable. The residence time in mixer-settler extractors will depend on the number of stages and the rate of coalescence of the dispersed phase at each stage. In differential contactors, however, settling and phase separation take place at one of the ends of the column and will depend entirely on the mean droplet rising (or falling) velocity.

(iv) Phase flow-ratio. Mixer-settlers are preferable to differential contactors at high phase ratios, since the dispersed phase hold up in differential contactors is a fraction of the phase ratio and hence, the performance decreases as this ratio decreases.

(v) Physical properties. The drop size in nonagitated differential extractors is a function of the parameter $(\frac{\sigma}{\Delta\rho})$, the larger the value of this parameter, the smaller the interfacial area and therefore the poorer the mass transfer performance and eventually agitated contactors have to be used instead.

(vi) Phase dispersion and hold up. It is usually preferred to disperse the phase with the highest throughput in order to obtain the maximum contact interfacial area. When low hold up of one of the phases is desirable, minimum residence time and contactor volume are required. These requirements can be best provided by centrifugal contactors.

(vii) Presence of solids. For most type of extractors, the presence of solids in one or both the feeds would necessitate periodical shutdowns to remove the solid deposits. Mixer-settlers are usually more flexible in handling this problem.

4.2.2 Equipment for Phosphoric Acid Purification

When evaluating equipment for the purification of wet process phosphoric acid, the following features favour the choice of mixer-settler extractors:

(i) The number of equilibrium stages required is usually small. In addition the concentration gradient is normally large from stage to stage, which renders the process very sensitive to back-mixing effects.

(ii) As the solvents considered are partially miscible with water, there may be significant changes in the physical properties and volumetric flow rates of the phases from one stage to the next, necessitating mixing and phase separation in each stage.

(iii) The need to provide for the introduction and removal of side streams.

(iv) The need for flexibility of flow-sheet configuration, by removal or addition of contact stages. This flexibility is especially important when operating with varying grades of phosphoric acid.

(v) The scale-up of mixer-settler contactors is more reliable than that for differential devices.

(vi) Mixer-settler arrangements can be started up rapidly, by filling the equipment in a cross-current fashion.

(vii) On shut downs, the contents of each mixer-settler stage remain at equilibrium; thus steady state operation can be resumed immediately without loss of time and production of off specification product.

4.3 MIXER-SETTLER ARRANGEMENTS

Mixer-settler equipment can be arranged vertically or horizontally for countercurrent extraction. It may consist of one or more stages, each stage comprising a combination of a mixer and a settler. A large variety of mixer-settlers have been proposed. These may be classified into three types according to the manner by which the flow of liquid through the unit is brought about;

(i) Gravity flow type; in which the driving force for the liquid flow in each phase is the head between the inlet and outlet. In this case the hydraulic connections between the vessels must be sufficiently wide in order to minimize the flow resistance. However, by increasing the cross-sectional area of the connections between the vessels, the danger of back-mixing is equally increased.

(ii) Interstage-pumping type. The flow of one or both of the liquids is brought about by pumping between stages. This makes the unit more complicated and increases the power consumption and maintenance costs.

(iii) Pump-mixing type. The pumping of liquid between stages is combined with mixing in the mixer, and therefore, the intensity of mixing will depend largely on the flow rate.

Vertical arrangements of mixer-settlers generally incorporate a common shaft for agitation and the transfer of liquid is nearly always achieved by gravity, while in horizontal

arrangements, the transfer of liquid is achieved by any of the three methods described above.

Successful designs of mixer-settler units should provide reasonably high stage efficiency, include simple interface control, provide continuous movement of the two phases and the unit should be mechanically simple and reliable in operation.

4.4 THE PHASE DISPERSED

The extraction rate, the equipment size and the power requirement for a particular extraction operation may be affected by which of the phases is dispersed in the resulting dispersion (54). Either liquid can be made continuous by starting agitation in the liquid present and then adding the liquid to be dispersed. Quin and Sigloh (55) stated that the type of dispersion depends on volumetric ratio of the two liquids, their physical properties and the dynamic characteristics of the mixer. They found that phase inversion can take place by changing the impeller geometry and the rate of energy input. Selker and Sleicher, Jr.(54) found that the viscosity ratio of the two phases has a great effect on deciding which of the phases will be continuous within the ambivalent volume range. This range is defined as the range of volume fraction within which either phase may be continuous (0.26 to 0.74). Rodger and Trice (25) noticed with most of the systems they studied that the stable dispersion at low energy input was oil/water (O/W), but as the energy input was increased phase inversion took place, which

was always accompanied by a change in settling time. They also found that as the value of $\frac{\Delta\rho}{\rho_f}$ was made larger, it became easier to cause phase inversion and with systems having $\frac{\Delta\rho}{\rho_f}$ values of the order of 0.6, O/W dispersion were not possible to produce unless the position of the impeller was changed.

Quin and Sigloh (55) used a conductivity probe to determine which phase was continuous. Dyes that are either oil or water soluble can be also used (54) for this purpose, but their addition may affect the behaviour of the dispersion since most dyes are surface active. Another visual method to determine the continuous phase is by examining the manner in which the dispersion settles out (25, 54).

4.5 STAGE AND STAGE EFFICIENCY

A stage consists of a single or combination of devices in which the extraction occurs on mixing, and the resulting liquid phases are settled and separated. When the separated liquids are in thermodynamic equilibrium, the stage is said to be ideal or theoretical. The fractional approach to equilibrium that may be attained by the liquids from an actual stage is then the stage efficiency, and this may be expressed in many ways. The Murphree stage efficiency is frequently used, it measures the approach of the effluent streams to equilibrium, thus for a final extract which is discharged with concentration Y_2 and for which equilibrium concentration with a raffinate, X_2 is Y_2^*, the Murphree extract stage efficiency is

$$E_{ME} = \frac{Y_2 - Y_1}{Y_2^* - Y_1} \qquad (4.1)$$

Similarly, for the raffinate, the Murphree stage efficiency is

$$E_{MR} = \frac{X_1 - X_2}{X_1 - X_2^*} \qquad (4.2)$$

Where X_2^* is the raffinate in equilibrium with extract at Y_2. The overall efficiency of a cascade of stages is the ratio of number of ideal to actual stages required for a given concentration change

$$E_o = \frac{n}{n_r} \qquad (4.3)$$

Overall stage efficiencies for cascades of the mixer-settler type have been reported (47) ranging from 0.75 to 1.0. On the other hand stage efficiencies near to 1.0 can be obtained with agitated vessels. Overall stage efficiencies less than 0.75 may be the result of incomplete settling (entrainment) or because of other backmixing effects.

Flynn and Traybal (48) investigated the effect of vessel size, rate of flow, agitator speed and power, and phase ratio on the stage efficiency of agitated extractors. They concluded that the agitator power per unit volume of total liquid flowing may be the most important factor affecting stage efficiency, since it increases exponentially with agitators speed. Beyond a certain optimum speed, Coplan et al (49) reported that the stage efficiency decreased and in addition made separation more

difficult. The decrease in efficiency was attributed to the change in mass transfer characteristics, since the drops cease to oscillate or possess internal circulation, and become rigid when their diameter is reduced beyond a certain limit.

Overchashier et al (42) used the following relationship for the countercurrent stage efficiency,

$$E = \frac{\log\frac{(mY_2 - X_2 + b)}{(mY_1 - X_1 + b)}}{\log\frac{(mY_2 - Y_1)}{(X_2 - X_1)}} \qquad (4.4)$$

where m is the slope of equilibrium line and b is the intercept of equilibrium line.

4.6 MIXER SETTLER EQUIPMENT

A wide range of mixer-settler equipment is available, in which the extraction process may be batchwise or continuous. They may be placed in the following categories (17):

I. Mixers

A Agitated Vessels

(i) Mechanically agitated

(ii) Gas agitated

B Flow or Line Mixers

(i) Mechanically agitated

(ii) Not agitated

II Settlers

A Non-mechanical

(i) Gravity

(ii) Centrifugal (cyclones)

II Settlers (continued)

B Mechanical (centrifuges)

C Settlers Auxiliaries

(i) Coalescers

(ii) Separator membranes

(iii) Electrostatic equipment

In principle at least, any of the mixers may be used with any of the settlers in continuous extraction.

4.6.1 Mixers

The optimum design of a mixer for a particular extraction, should establish the best shape and size of the vessel, method of agitation, internal construction and power consumption to attain the best extraction rate with the least cost.

4.6.1.1 Agitated Mixers

Mechanically agitated vessels are the most important and widely used mixers. They are usually vertical cylinders with a smooth internal surface. They may be fitted with internal baffles, which are necessary to prevent vortexing and in directing the circulation currents. Impellers are usually placed on vertical axial shafts with the exception of propellers in unbaffled vessels, where they have to be located away from the centre of the vessel to avoid vortexing. Propellers have been used for low viscosity liquids and they produce axial flow. Turbines and paddles produce radial flow if vertical baffles are used and rotational flow about the impeller shaft if the vessel is unbaffled. Details of the various impellers are given in

references (17) and (50).

Gas agitation has been considered an inefficient method of mixing, and only a little is known about its effectiveness for mixing immiscible liquids (51). Mathers and Winter (52) utilised an air-lift pump principle for agitating immiscible liquids in which air is introduced at the bottom of the mixer through a nozzle, over which a vertical lift tube is placed for the liquid circulation. This, however, has the distadvantage of causing volatilization of the solvent and the possibility of undesired oxidation.

4.6.1.2 Flow or Line Mixers

Flow or line mixers are devices for bringing about dispersion of one liquid in another while they are being pumped through the apparatus. They have small volumes and consequently provide little holding time. They are especially useful for liquids of low viscosity and low interfacial tension, for which dispersion is not difficult. Flow mixers can be classified into four basic types (17).

1. Jets, or devices depending upon impingement of one liquid upon the other for intimate mixing.
2. Injectors, where the flow of one of the liquids is induced by the flow of the other, at the same time resulting in mixing.
3. Orifices and nozzles, which bring mixing and dispersion by causing turbulance when both liquids are pumped through the device.

4. Flow mixers with mechanical agitation.

Generally, flow mixers are inexpensive to instal, but may produce high pressure drop and consequently may be expensive to operate. More information about flow mixers can be obtained from reference (17).

4.6.2 Settlers

The dispersion from the mixer, in continuous extraction, is allowed to flow through a settler of sufficient size to attain phase separation. Before discussing the design and performance of various types of settlers it is worthwhile considering the behaviour of emulsions produced when mixing immiscible liquids.

4.6.2.1 Emulsions and Dispersions

The stability, or permanence, of the emulsion is clearly a very important property, since it is necessary to separate the phases at each extraction stage. Stability represents the resistance offered by dispersion to coalescence of the dispersed phase droplets. For an emulsion to "break" or separate into its phases in bulk, both sedimentation and coalescence of the dispersed phase must occur.

The rate of sedimentation is faster if the droplet size and the density difference of the liquids are large and if the viscosity of the continuous phase is small. Stable emulsions, those which settle only over long periods of time, are usually formed when the diameter of the dispersed phase droplets is of the order of 1 to 1.5 microns. Other factors also contribute

to emulsion stability such as the presence of surface active agents and electrolytes.

The rate of coalescence of settled droplets is more rapid at high interfacial tension. Ordinarily the interfacial tension is low for liquids of high mutual solubility and is lowered in the presence of emulsifying agents. With a high viscosity continuous phase, the rate of coalescence is low because the rate of drainage, thinning and removal of the film between the droplets is reduced. Therefore temperature changes have a strong influence on the coalescence rate (53) since it affects both viscosity and interfacial tension.

Unstable emulsions settle and coalesce rapidly, after agitation is stopped, into two liquid phases (primary break), unless the viscosity is high. One phase, ordinarily that in the majority, may remain clouded by a very fine haze or fog-like dispersion of the other phase. The cloud will eventually settle out, leaving both layers clear (secondary break), although this may take a considerable time. It is usually impractical, in continuous multistage operations to hold the mixtures between stages long enough to attain the secondary break. However, for the purpose of conserving the solvent, it may be necessary to clarify as completely as possible the settled phases from the final stage of a cascade.

4.6.2.2 Settler Equipment

The economic efficiency of a settler lies in obtaining phase separation at the lowest entrainment level possible in

each discharged stream, with the minimum erected equipment cost, the most compact layout and the smallest volume (to minimise the solvent inventory cost). On the other hand, since good phase separation results are critical for plant operation and since settler behaviour is not generally understood or predictable with changing conditions (56), generous design safety factors are usually introduced. The general description of settlers in common use are given below.

4.6.2.2.1 Gravity Settlers

Gravity settlers are widely used in the chemical industry. The simplest type is usually a horizontal vessel, which may be fitted with either slotted or perforated vertical baffle at the settler's inlet to protect the vessels contents from disturbance by the jet of entering dispersion. The bulk of the settler is used to provide a nonturbulent flow regime to obtain rapid settling. Phase separation is characterized by a dispersion band at the interface which decreases in thickness as the liquids move towards the other end of the settler. If the flow rate of the entering dispersion is increased, the layer of unbroken dispersion increases in thickness until eventually unsettled dispersion leaves with the discharged streams. Ryon et al (57) reported that the thickness of the unbroken dispersion band increases exponentially with increasing flow until the settler is flooded. They recommended that for a chosen dispersion flow rate and length of settler, the cross-section for the prevailing flow rate should be set to twice the value that would give a

dispersion band thickness equal to the depth of the tank. Jeffreys et al (58) in a study of dispersion separation in a single mixer-settler unit, reported that the dispersion band in the settler was wedge shaped and its length increased with increasing dispersed phase flow rate and decreasing inlet drop diameter.

There are hundreds of variations of the simple gravity settler. Vertical, rather than horizontal, cylinders are used in some cases, and advantages have been claimed when they are put at an angle to the horizontal. The admission of the liquid mixture is generally preferred to be at the level of the interface. Baffles of various descriptions are frequently used to influence the direction of flow, to cause impingement of the dispersion, to ensure laminar flow and to reduce the distance through which the droplets must settle and coalesce.

4.6.2.2.2 Cyclones

Cyclone settlers offer the advantage of low residence time to achieve phase separation which results in a reduction of the equipment size, minimum solvent inventory and in some cases provides processing advantages. However, it is not widely used for liquid-liquid applications in industry because generally good clarification of both effluents cannot be obtained in one cyclone (59). However, complete phase separation can be achieved in two cyclones (60), but this requires additional pumping for recycling.

4.6.2.2.3 Centrifuges

Centrifuges are mechanically rotated settlers which allow rapid continuous sedimentation of the dispersion even at low values of density difference of the two phases. There are two major types, the hollow-bowl centrifuge and the disk-bowl centrifuge. Either type may be designed for separating solids as a concentrated slurry in one of the liquids. Centrifgues are expensive machines and are generally limited to cases where low separation holding time is essential and where phase separation is difficult.

4.6.2.2.4 Settler Auxiliaries

These may be added to the settler. They will generally enhance coalescence of the dispersed phase droplets and they include coalescers, separating membranes, electrical devices and the addition of emulsion breaking reagents.

CHAPTER FIVE

FLOW-SHEET DELINEATION AND PROCESS OPTIMIZATION

The complete economic design of an extraction process for the purification of phosphoric acid is too complex to be considered in this study. However, after testing the project feasibility, profitability and risk, a more detailed design of the plant units, to establish the optimum conditions, may be undertaken independently.

The extraction process envisaged in this work is the purification of wet-process phosphoric acid and the proposed flow diagram is presented in fig. 5.1. Once the product requirements have been defined, the solvent selected and the equilibrium data determined, it is possible to outline and optimize the flow sheet. Such optimization is aimed at the determination of those operating conditions which result in the minimum annual manufacturing cost (including both capital and operating costs).

5.1 FLOW SHEET DESCRIPTION

The proposed flow sheet for the purification of wet-process phosphoric acid is presented in fig. 5.1. The stream flow rates are expressed in tons/day on a solute-free basis and their concentrations are expressed in tons of solute per ton of solute free liquor. It is assumed that the extracting

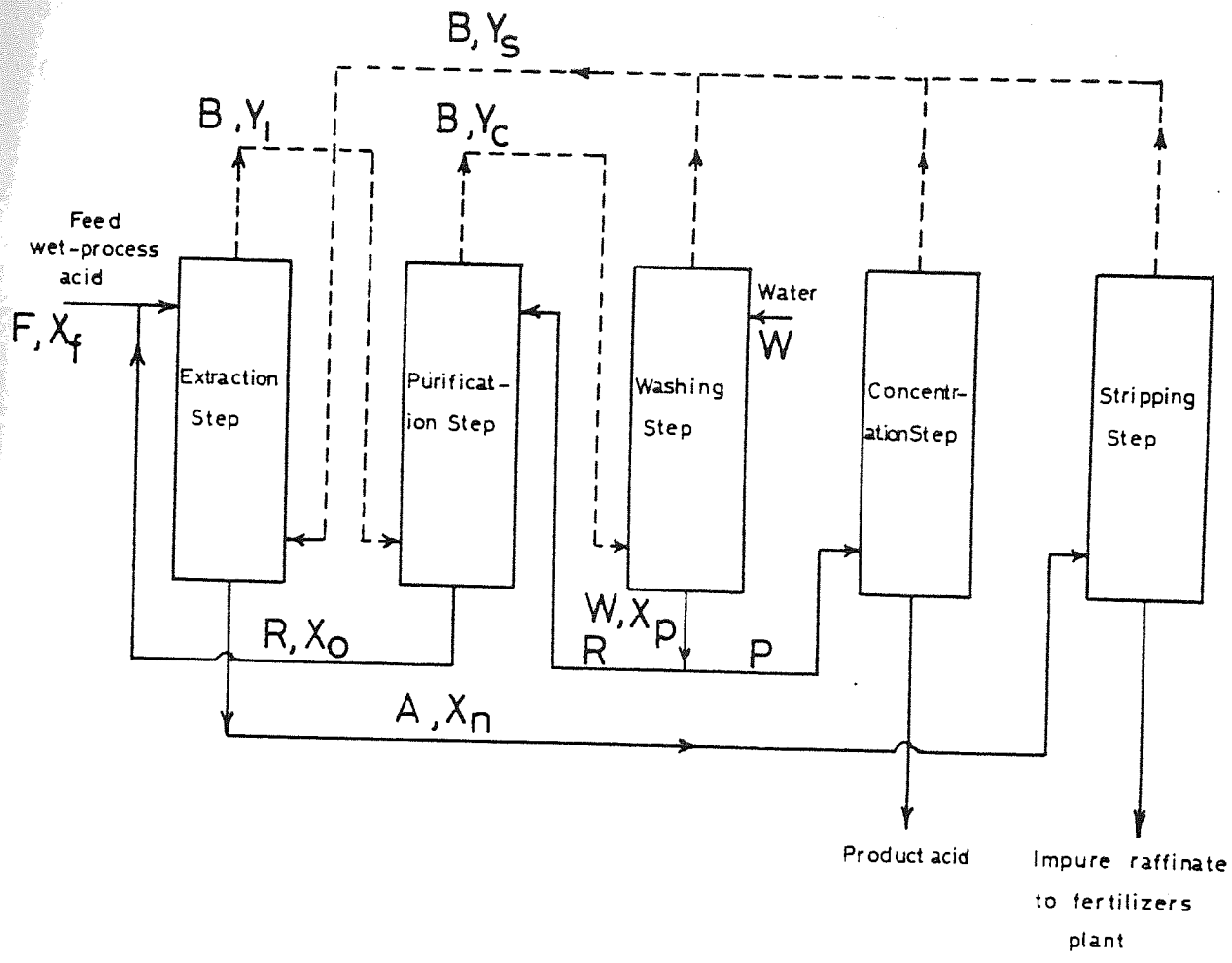


Fig. 5.1 General flowsheet of the Purification Process envisaged

solvent is immiscible with the carrier liquor of the feed (water).

In this process the combined feed stream at a flow rate (A) and a H_3PO_4 concentration (X_A) is contacted in a countercurrent multistage extractor with a solvent at flow rate (B) and H_3PO_4 concentration (Y_s). After separation of the phase the raffinate, at a flow rate (A) and H_3PO_4 concentration (X_n) flows for treatment to the stripping section and then to a fertilizer plant where it can be used to produce fertilizer grade phosphates. The extract phase at a flow rate (B) and H_3PO_4 concentration (Y_1) passes to the purification step where it is contacted in a countercurrent multistage contactor with a recycle of product acid at a flow rate (R) and H_3PO_4 concentration (X_p). The purified extract phase at flow rate (B) and H_3PO_4 concentration (Y_c) passes to the washing step in which the acid is extracted back into water. The recovered solvent is recycled to the extraction step and part of the product to the purification step. The other part of the product at a flow rate of (P) and concentration (X_p) can either be used directly or further concentrated if required. However, it is possible that with some solvents the product will have to be treated to remove the small percentage of solvent remaining.

Accordingly the flow sheet presented in fig. 5.1 can be divided into five steps and the functions of each step can be summarised as follows:

I. Extraction Step: The aim here is to extract phosphoric acid and separate it as much as possible from its impurities. This step comprises a number of countercurrent liquid-liquid contact stages.

II. Purification Step: The extract phase from the extraction step is contacted in a countercurrent multistage contactor with a recycle stream from the phosphoric acid product with the primary objective of purifying the extract by extracting its impurities into the phosphoric acid. Because of the inclination of the tie lines, this step could also act as the rectification section in a countercurrent extraction with reflux, and therefore if the phosphoric acid recycle is of a higher concentration than that which will be in equilibrium with the contacted extract, mass transfer will take place with resulting increased phosphoric acid concentration in the extract. However, the enriching of the extract is limited by the availability of a high grade phosphoric acid product and the fact that the transfer of impurities into the recycled stream becomes more difficult as its acid concentration increases.

III. Solvent recovery (Washing) Step: This is the true counter part of the extraction step. Here the purified extract from the purification step is contacted, in a countercurrent contactor with water where phosphoric acid is extracted into water. The regenerated solvent is recycled in the process.

IV. Concentration Step: In this step the pure acid is concentrated, if required, to a marketable grade. This is done by evaporation which will also serve for the recovery of dissolved solvent.

V. Raffinate treatment (Stripping) Step: The raffinate may be vapourised to recover solvent after which the impure acid is pumped to a fertilizer plant.

5.2 PROCESS OPTIMIZATION

Process operations can usually be modelled using mathematical equations describing the relations between the independent and the dependent variables of the process and therefore the optimization of any objective function becomes purely a mathematical problem. This involves the construction of mathematical models with suitable parameters and boundaries. Then devising methods of solving the equations for the optimized quantity in terms of the controlled independent variables of the process.

The purification of wet-process phosphoric acid by liquid extraction is no exception. When it is required to minimize the total annual manufacturing cost of a certain quality product under a given set of process parameters it is necessary to define the individual costs contributing to the total cost. These may be defined in terms of the controlled variables, such as phase ratios of the different extraction systems and level of acid concentration in the raffinate and recycled solvent.

The determination of every possible condition and design factor that would result in the optimum purification plant may require a very long series of design and cost computations. However, by making a few reasonable assumptions, approximate optimum conditions can be determined relatively quickly. The detailed analysis is then only required in that neighbourhood of the optimum region to determine the exact optimum conditions.

5.2.1 The Objective Function

The objective function of the envisaged process is defined as the total annual manufacturing cost per ton of P_2O_5 in the product at a fixed output capacity of Tons P_2O_5 per day. This total cost is to be minimized for each solvent. The cost is determined by a set of process parameters and may be taken as the sum of seven individual costs:

$$C_T = I + II + III + IV + V + VI + VII \qquad (5.1)$$

where

C_T = Annual total cost of the purification process.

I = Annual cost of the extraction step

II = Annual loss in value of raffinate as wet-process acid lower in H_3PO_4 concentration and richer in impurities added to annual cost of raffinate treatment for solvent recovery.

III = Annual cost of the purification step.

IV = Annual cost of the solvent recovery (washing) step.

V = Annual cost of the lost solvent.

VI = Annual cost of product concentration.

VII = Annual cost of labour.

The annual cost of labour will be considered constant and therefore item VII is not subject to optimization.

The above analysis has to be repeated for different solvents and process parameters if an overall optimum is required. The various cost items will be defined in detail later (Chapter 8) after enough information about the systems has been developed.

5.2.2 Optimization Methods

Optimization methods are numerous, but they can be grouped into two types - indirect methods and direct methods.

5.2.2.1 Indirect Methods

These are also called analytical methods. They are only applicable when the objective function is differentiable with respect to the independent variables. The necessary condition for a minimum or a maximum of a function f(x), when all the first partial derivatives $\frac{\partial f}{\partial x_i}$, i = 1,.....,n, exist at all points is that

$$\frac{\partial f}{\partial x_1} = \frac{\partial f}{\partial x_2} = \frac{\partial f}{\partial x_n} = 0 \qquad (5.2)$$

Solution of the above equations simultaneously should provide the values of the independent variables x_i at the optima. However, a sufficient condition for a point satisfying these equations to be a maximum or a minimum is that all

the second partial derivatives $\frac{\partial^2 f}{\partial x_j \partial x_k}$ (j,k=1,.....,n) exist at this point and that when Di for i=1,2,.....,n is positive the function at the point is a minimum and when negative it is a maximum, where

$$Di = \begin{vmatrix} \frac{\partial^2 f}{\partial x_1^2} & \frac{\partial^2 f}{\partial x_1 \partial x_2} & \frac{\partial^2 f}{\partial x_1 \partial x_i} \\ & & \\ \frac{\partial^2 f}{\partial x_i \partial x_1} & & \frac{\partial^2 f}{\partial x_i^2} \end{vmatrix} \qquad (5.3)$$

Although, the analytical approach is the only one which will yield information on all stationary-point locations within the region, such methods suffer some major practical disadvantages. In general, the determination and solution of the set of non-linear equations (5.2) presents considerable difficulty. The solution of equations (5.2) does not necessarily represent the required minimum or maximum, it could represent a local minimum a local maximum or a saddle point. Test of the objective function at all stationary values, however, should reveal the desired type of optimum. A further limitation of this analytical approach is that it is not readily applicable to functions with discontinuous derivatives (61), although this can be handled by the use of additional restrictions at each discontinuity (62) which will generally include the possibility of the optimum solution lying on the boundary of the valid region.

5.2.2.2 Direct Methods

Direct optimization methods are more commonly used, they are also called iterative methods because the application of iterative techniques. Such techniques require an initial point X_o to be specified, and proceed by generating a sequence of points X_i, i = 1,2,.....; which represent improved values of the objective function. Direct methods may be subdivided into two classes:

i) Direct search methods. These do not require the explicit evaluation of any partial derivatives of the function, but instead, they rely entirely on values of the objective function at given points, plus information gained from earlier iterations. Some of these methods, however, use the values of the objective functions to obtain numerical approximations of its derivatives or to fit low order polynomials or surfaces through selected points (62).

The basic difference between the various direct search methods is the way they choose the direction for the second feasible location. Generally, there are two ways, the first is by directing the search in some pattern move such as a regular geometric figure as in the simplex method (63) in which the objective function is evaluated at the points formed by the vertices of the geometric figure. The vertex at which the function's value is worst is rejected and the general direction of the search may then be taken away from this point. The second way is by directing the search in directions parallel to

some vectors related in number to the number of the independent variables. The simplest of these methods is by directing the search parallel to the coordinate axes, (sectioning method) (61) in which only one variable is changed at a time while the others are kept constant. The search along each direction can be conducted by one of the linear search methods such as Fibonacci technique (61), the algorithim of Davies, Swann and Campey (62) or by Powell's algorithm (62). Sectioning method is considered to be inefficient especially when the contours of the system come to a sharp point, where the method tend to oscillate with steadily decreasing progress towards the optimum. Other methods based on the same principle have been developed and are more efficient since they utilize better the information gained from early iterations to find better directions towards the optimum. More than one variable is changed at a time in techniques such as Hooke and Jeeves' Method (64), Powell's method (65) and Rosenbrock's method (66).

ii) Gradient search methods. In these methods (61) on the other hand the best direction to locate the optima is selected by evaluating the partial derivatives of the objective function with respect to the independent variables, as well as the objective function itself, together with information gained from earlier iterations. Gradient methods, can generally be divided into two categories. The first group follows the direction of the steepest ascent as closely as possible while the second uses the gradient to guide the search but the moves are not necessarily in the direction of the steepest ascent.

In general, the selection of the most efficient direct method of optimization is difficult since each optimization problem has its own characteristics which will usually depend on the function itself. However, if the derivatives of the objective function are not given in explicit terms, a direct search method is usually selected. While the simplex method is simple to program, it does not converge as quickly as some of the other more powerful direct search techniques such as the Rosenbrock technique and the Powell technique. The latter method exhibits quadratic convergence and was claimed by Box, Davies and Swann (62) to be the most effective direct search method. It can be used in conjunction with one of the linear search methods to accelerate the location of optima along the direction of search. If the objective function gradients are easily evaluated, for example, from an analytical expression, gradient methods should be used in preference to direct search methods since they are more powerful and rapid in their convergence.

However, both types of direct optimization are subject to the same weaknesses. Because of their iterative nature, convergence is usually a major difficulty but this varies, depending on the system and the particular method applied. Also these methods can not guarantee the global optima of a non-unimodal objective function. This problem can be overcome with some degree of confidence by starting the search at different initial base points. If several optima are found

the best is selected. The presence of constraints on the independent variables may cause further difficulty in the optimization procedure.

5.2.2.3 Optimization Methods Previously Applied to Solvent Extraction Processes

Although some work has been done in optimization of cross-current solvent extraction processes (67, 68, 69, 70, 71) which is mostly based on the discrete maximum principle, very little has been published on countercurrent solvent extraction processes and none on those with reflux, similar to the process described in this work. Salem (75) used the discrete maximum principle in optimizing a countercurrent solvent extraction process, while Mitten and Nemhauser (72) applied dynamic programming for the optimization of countercurrent mass-transfer operations. Jenson and Jeffreys (73) studied the effect of the number of contact stages and the flow rate of the extracting solvent on the cost of countercurrent and cross-current extraction processes and developed some generalised charts for the optimization of the process. Jeffreys et al.(74) used the Hooke and Jeeves direct search method and the indirect method for the optimization of a solvent extraction process in which the solvent is recovered by distillation and from a comparison between the results they obtained by both methods it was indicated that the total optimum cost (C_T) predicted by the first method was around 15% lower that that obtained by the second method. This may be due to the assumptions made in solving the differential equations.

For the optimization of the process envisaged in this work, the Powell method will be used as a direct search method accompanied by the use of the Algorithm of Davies, Swann and Campey as a linear search method for the location of the optima along the vector directions. The choice of these methods was based entirely on their good reputation (62). Along with this direct method, attempts to optimise the process by the indirect methods were carried out and proved to be unsuccessful because of the difficulty in solving the resulting equations as will be shown in Appendix (IV).

5.2.2.4 Powell's Optimization Method (65)

This method is based on the generation of conjugate directions through which the location of the optima is accelerated. For a quadratic function to be optimized written in the matrix-vector notation as

$$f(X) = \tfrac{1}{2}X'GX + b'X + c \qquad (5.4)$$

the directions ε_i and ε_j are said to be conjugate with respect to G if

$$\varepsilon_i G \varepsilon_j = 0, \quad \text{for } i \neq j$$

Starting from the best known point X_o to the optimum, the optimization procedure commences by searching through n linearly independent directions $\varepsilon_1, \varepsilon_2, \ldots\ldots, \varepsilon_n$. The search to locate the best point in any direction can be performed by one of the linear search techniques such as the algorithm of

Davies, Swann and Campey. Generally the initial n directions chosen are coordinate directions, so the start of the first iteration is identical to an iteration of the sectioning method which changes one variable at a time. Powell's method generates conjugate directions by making each iteration define a new direction ε and choosing the linearly independent directions for the next iteration to be $\varepsilon_2, \varepsilon_3, \ldots, \varepsilon_n, \varepsilon$. After n iterations all the directions should be mutually conjugate and for a quadratic function the optimum should have been located. But since, in most practical problems the objective function is not quadratic, convergence cannot be assured in an n number of iterations. However, most functions approach quadratic behaviour (61) in the neighbourhood of their optimum and therefore quadratically convergent methods can be considered effective in optimizing non-quadratic objective functions.

A modified form (65) of Powell's method is summarised below for n independent variables. The illustration of fig. (5.2) is for two variables.

1. Starting with the best previous value position $X_o^{(k)}$ and a series of independent directions $(\varepsilon_1^{(k)}, \varepsilon_2^{(k)}, \ldots, \varepsilon_n^{(k)})$ (usually coordinate axes at the first start when k = 1), begin the search using a linear search method to find the optimum position along the line passing through $X_o^{(t)}$ which is parallel to $\varepsilon_1^{(k)}$. From this optimum point $X_1^{(k)}$, begin a second search in the $\varepsilon_2^{(k)}$ direction. The procedure is continued

until all n search directions have been explored and hence one iteration is finished.

2. Find the particular point $X_m^{(k)}$ for which the greatest improvement in the objective function Δ over its previous value is achieved.

$$\Delta = |f(X_m^{(k)}) - f(X_{m-1}^{(k)})| \qquad (5.5)$$

Also determine the vector $\varepsilon = X_n^{(k)} - X_o^{(k)}$

3. Determine $f(2\,X_n^{(k)} - X_o^{(k)}) = f_3$ and define $f_1 = f(X_o^{k})$ and $f_2 = f(X_n^{k})$.

4. If, in seeking a minimum

$$f_3 \geqslant f_1$$

and/or

$$(f_1 - 2f_2 + f_3).\ (f_1 - f_2 - \Delta)^2 \geqslant \tfrac{1}{2}\,(f_1 - f_3)^2$$

then ε is not a good direction to introduce into the set of directions of search. In that case begin the search again, using the old directions, starting from the last point, $X_o^{(k+1)} = X_n^{(k)}$. If neither of the conditions is satisfied search along the direction ε until the optimum is found and start from this point $X_o^{(k+1)}$ and the new directions for the (k+1) stage will be $\varepsilon_i^{(k+1)} = \varepsilon_i^{(k)}$, $i = 1, \ldots, m-1$; $\varepsilon_i^{(k+1)} = \varepsilon_{i+1}^{(k)}$, $i = m, \ldots, n-1$; and $\varepsilon_n^{(k+1)} = \varepsilon$. The entire procedure is repeated starting from 1.

Because of the modification which allows the old set of linearly independent variables to be used again, the method may not necessarily be quadratically convergent since one or more of the mutually conjugate directions might be discarded and therefore, more than n iterations would be required to find the exact optimum of a quadratic function. Despite this, the modification has been claimed by Powell (65) to be of value and was found essential when optimizing functions of twenty variables.

5.2.2.5 The Algorithm of Davies, Swann and Campey (62)

This is a linear search method which finds the optimum along one direction. A typical situation for a minimization case is illustrated in fig. 5.3. After evaluating the function at the previous best known position, a step is made along the direction of search, and the function is recalculated. If this function value is improved or equal to the initial function value, the step length is doubled, and the search is continued in the direction in which the function is improving. This process is repeated until a step resulting in a worsening of the function is realised, indicating that the optimum has been overshot. The step-length is then halved, and a step is taken backward from the last point. This will give four points equally spaced, at each of which the function has been evaluated. The end point furthest from the point corresponding to the best function value is rejected and the three remaining points are used for quadratic interpolation.

The numbers in fig. 5.2 refer to the sequence in which the points were introduced and in this particular example the points 4, 5 and 6 would be used for the interpolation.

If the first step fails, the direction of search is reversed and the procedure outlined above is again followed. If the first step in the reversed direction also fails, then the optimum lies within, and interpolation may be performed on the three points.

If the three points (along the direction of search m) used for interpolation were X_1, $X_2 = X_1 + S$ and $X_3 = X_2 + S$, where S is the step-length and the corresponding function values are f_1, f_2 and f_3. Then the optimum of the fitted quadratic lies at $X_2 + S_m$, where

$$S_m = \frac{S(f_1 - f_3)}{2(f_1 - 2f_2 + f_3)} \qquad (5.6)$$

The function is then evaluated at the new point $X_2 + S_m$ and the search is then begun with the original step-length along the next direction using as the initial point whichever of $X_2 + S_m$ corresponds to the best function value. The choice of the original step-length depends mainly on experience and the accuracy of the desired optimum. However the procedure programmed should enable the reduction of the original step-length at the final stage of optimization in order that the optimum within the desired accuracy can be reached sooner.

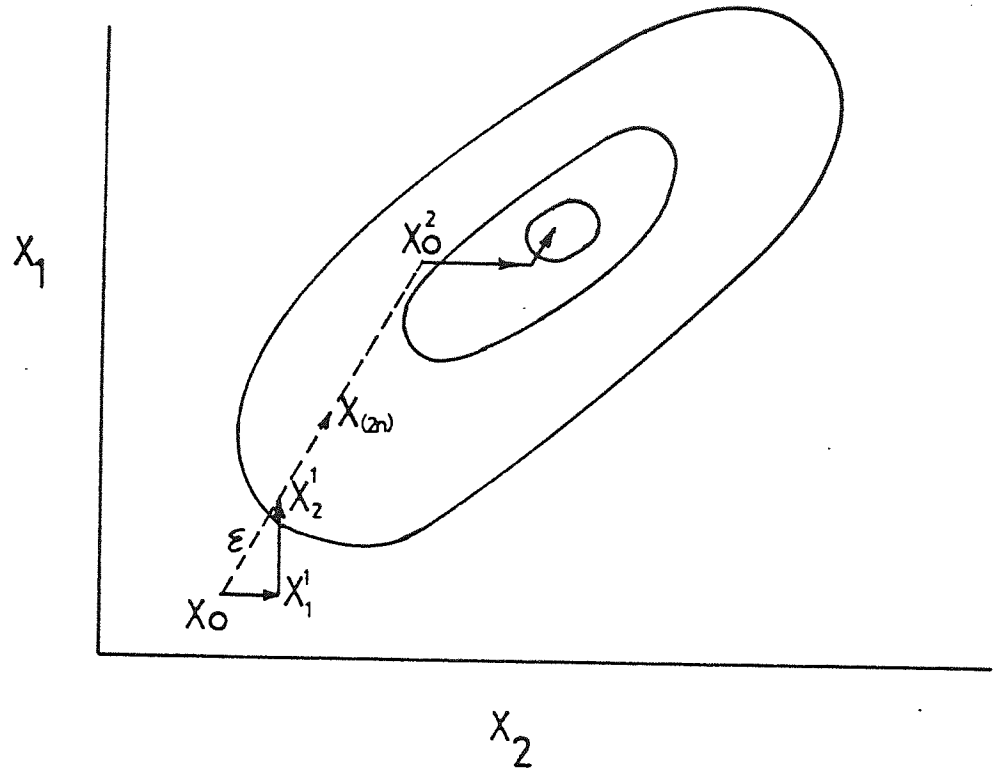


Fig. 5.2 Powell optimization of Two-dimensional problem

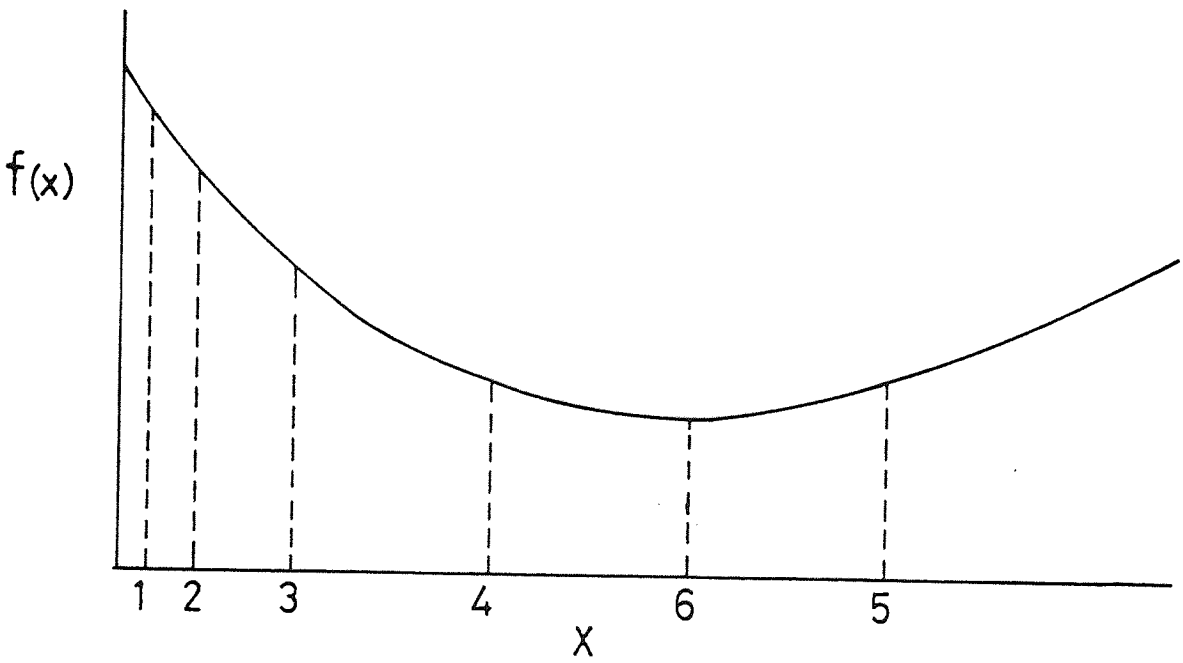


Fig. 5.3 The procedure of the algorithm of Davies, Swann and Campey

CHAPTER SIX

EXPERIMENTAL INVESTIGATION

6.1 OBJECT

The main objective of the experimental investigation was to evaluate promising immiscible solvents for the purification of wet-process phosphoric acid. This included the determination of phase equilibrium diagrams at 25°C for pure and impure systems containing iron, aluminium, calcium or magnesium; a study of the hydrodynamic behaviour of the various systems; applying and testing the knowledge gained on the purification of a wet-process acid; and using the information for the process development and optimization of the various purification systems.

The solvent systems envisaged were n-amyl alcohol, tri-n-butyl phosphate, di-isopropyl ether and methyl isobutyl ketone. The impurities used were in the phosphate salt form.

6.2 EQUIPMENT DESIGN AND CONSTRUCTION

The design of equipment and experiments was aimed at producing rapid and accurate information about a large number of systems. The equipment used for the determination of ternary phase diagrams can be divided into:

A. Equipment used for binodal curve determination by the cloud point. These are:

1. Large temperature controlled bath provided with a stirrer. The height of water in the bath can be varied from 5 to 20cm.

2. Clear glass measuring cylinders of capacities ranging from 50 to 100cc.

3. Precise 25ml burettes fitted with PTFE stop-cock; and liquid droppers.

4. Three-decimals (mgm) electrical balance.

5. Glass bottles of 200 - 300 ml capacity.

B. Equipment used for tie line determination. These are eight jacketted 300mls capacity glass cylinders, fitted with PTFE stop-cocks, operating batch-wise, and assembled as shown in figure 6.1 and diagramtically in figure 6.2. Each of these cylinders acted as a mixer-settler and is fitted with a Gallen-kamp stirrer of fixed rotation speed at 1200rpm, and supplied with constant temperature water from a thermocirculator (Churchill Co.) through the jacket to maintain constant temperature operation. The thermocirculator had a variable heat supply and could circulate 60 gal/hr at a temperature from -5 to 60^{o}C.

For the study of the hydrodynamic behaviour of the various systems the following set of equipment (figure 6.3) was used for

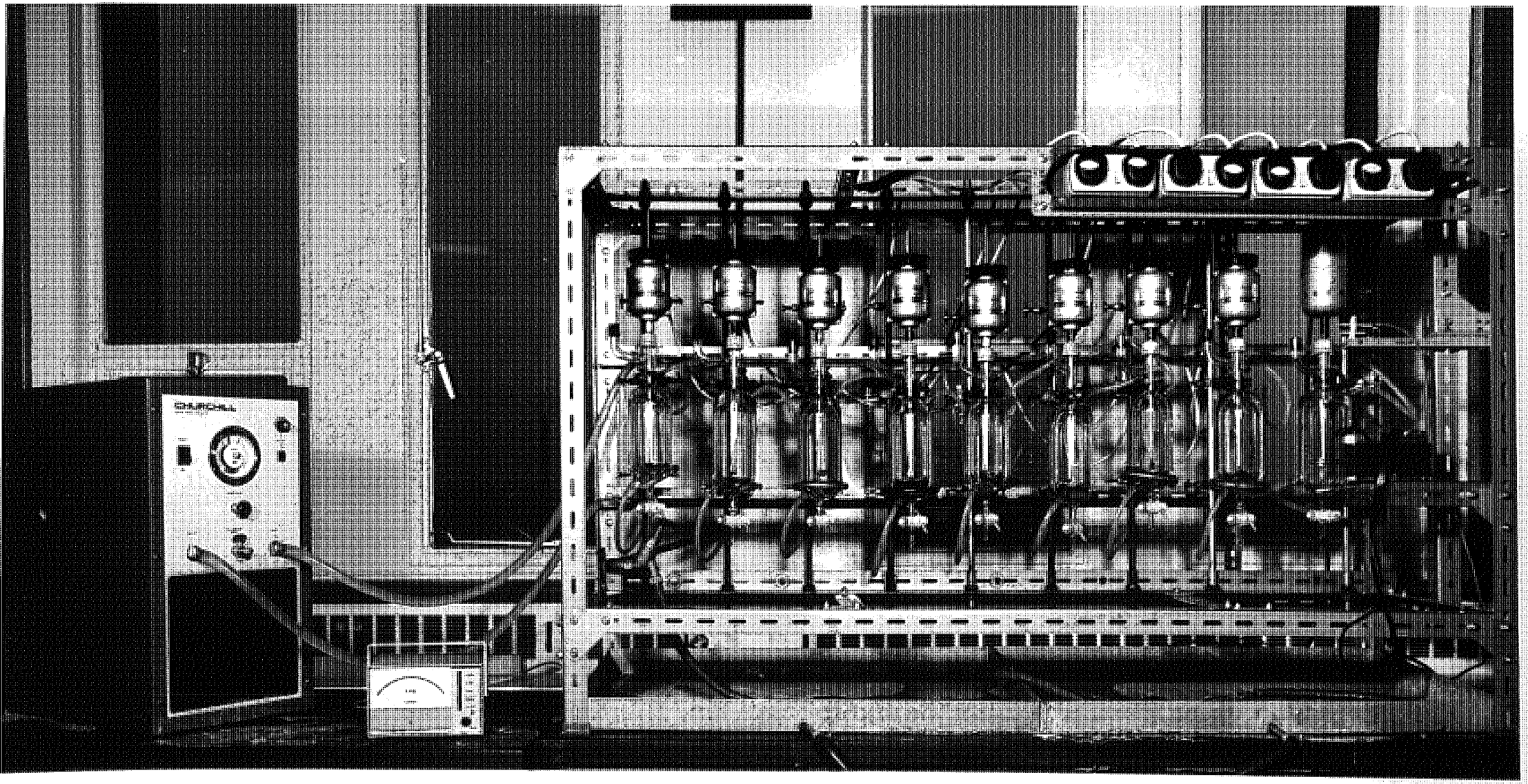


Fig.6.1. Jacketed cylinders assembly

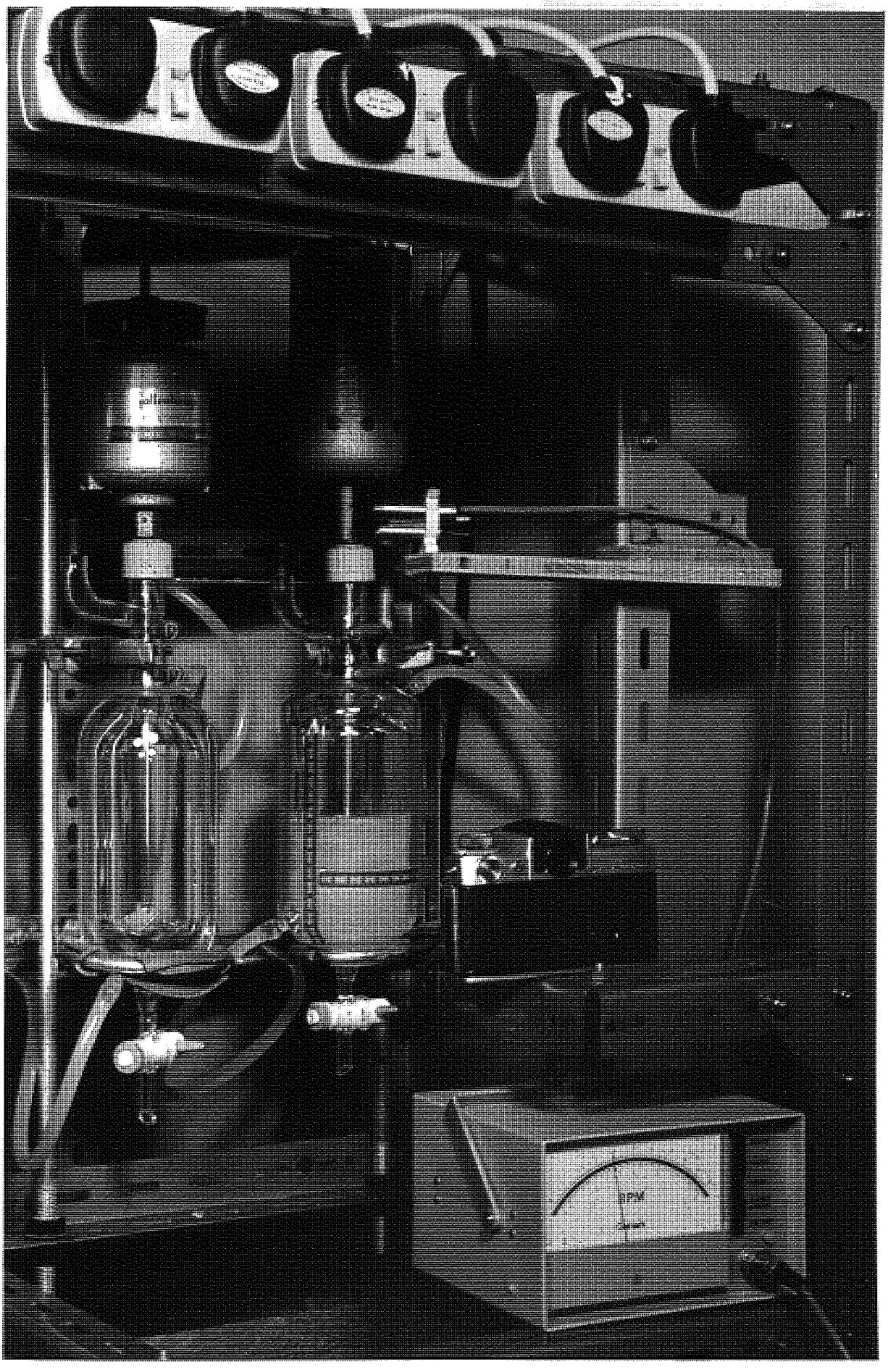


Fig.6.3. Hydrodynamic measurements equipment

drop-size distribution and coalescence measurements:

1. A jacketted cylinder of 6cm internal diameter and 14cm in height, as shown in figure 6.2., fitted with a variable speed stirrer (up to 4000 rpm). The stainless steel impeller is normally closed when stationary and has a diameter of 3cm, when fully opened (rotating), and a height of 1.5cm.

2. An Asahi Pentax Camera was used for still photography of the dispersion. An extension tube was attached to the camera for focussing at short subject distance. The distance between the camera and the cylinder was maintained constant using a spacing adaptor.

Lighting was provided by a 250 watt photoflood bulb placed behind the mixing-settling cylinder. Tracing paper was placed between the lamp and cylinder in order to diffuse the light. Kodak 35mm film, 400 Din was used throughout. In general, a shutter speed of 1/1000th of a second and an aperture of f5.6, f8 or f11 were found to give best results.

3. Electronic tachometer (Comark) for measuring the speed of agitation.

4. Stop-cock to measure the settling time and in some cases a cine camera of 8 frames/sec. was used to record the manner in which the dispersion coalesced.

The density, interfacial tension and some viscosity values

were also determined to provide adequate information for a quantitative interpretation of the system. These will be discussed in Section 6.6.

6.3 OPERATING PROCEDURE

When operating with systems containing phosphoric acid-water-solvent, when pure or containing an impurity as a fourth component, it is only possible to measure accurately H_3PO_4 and impurities when present. This led to the need for the determination of binodal curves and tie lines separately. The mixtures prepared for tie line determinations were mixed for 4 - 5 hrs at 25 $\pm$ 0.1°C. They were also used for drop-size distribution, coalescence and settling time, specific gravity, interfacial tension and viscosity measurements.

6.3.1 Determination of binodal curve

Known amounts of different concentration of solutions of H_3PO_4 in water were prepared in the measuring cylinders. Together with enough pure solvent they were separately stored for at least two hours in the controlled temperature water bath. The temperature of the liquids was checked periodically to make sure it was 25 $\pm$ 0.1°C.

A cylinder containing acid solution after its outside had been dried with a piece of cloth, was placed on the weighing balance. An exact known amount of the solvent was then dropped in from either a burette or a dropper. The cylinder was vigorously shaked and placed back into the bath. This procedure

was repeated until the single phase system was no longer clear but had become cloudy, so that further addition of a very small amount of solvent would result in the appearance of a second phase.

By determining the different cloud points, the water rich side of the binodal curve was determined. The same procedure was repeated to determine the solvent rich side of the binodal curve in which H_3PO_4 - solvent solutions were titrated against pure water, taking into consideration the amount of water already present with phosphoric acid.

With impure systems, the impurity was added in its phosphate form in an amount calculated to give 0.5% concentration of the element Fe, Al, Ca or Mg in the aqueous acid solutions. In some cases, especially with aluminium phosphate it was not possible to dissolve this amount and, therefore, the maximum possible amount was dissolved until saturation was almost reached. In the case of the solvent-rich side of the binodal curve, the solution of impurities in H_3PO_4 - solvent was not possible in some cases. The binodal curve was determined by titrating H_3PO_4 - solvent solutions with aqueous acid solutions (30 - 60% H_3PO_4) containing the required amount of impurity.

Heat was supplied to accelerate the solutions of aluminium phosphate and in some cases ferric phosphate. The solutions were then cooled down to the standard temperature. Since the amount of impurity was very small (less than 1.5% of total batch) in comparison with the other components, its weight was not taken

into consideration when constructing the ternary diagrams, i.e., they are on an impurity-free basis.

When evaluating H_3PO_4 - H_2O - di-isopropyl ether systems, pure and impure, a third layer (phase) appeared in a region of the ternary diagrams. The border of this region was defined using the same procedure mentioned above for finding the points at which a third layer would appear.

6.3.2 Tie Line Determination

A total of 200gm of aqueous acid solution and solvent mixture was prepared in such a proportion to produce 1:1 water to solvent by weight. Five different H_3PO_4 concentrations were prepared for each system, pure and impure containing 0.5% by weight (whenever possible) of the aqueous phase of one of the four impurities. A total of twenty-five mixtures, therefore, were prepared for each solvent. Eight of these mixtures at a time were mixed for 4 - 5 hours in the jacketed cylinder operating at 25 $\pm$ 0.1°C. The phases were allowed to settle in the cylinders. In turn, they were slowly withdrawan and transferred to the cylinder assigned for photographic measurements, after which the two phases were collected separately, weighed and samples were taken for the physical and chemical analysis.

The reason for maintaining 1:1 water to solvent by weight throughout, was to maintain experimental similarity between drop-size and settling time measurements. However, this meant that the relative volumes of the two phases (extract and

raffinate) was not constant throughout the various experiments but varied roughly within the range of 40 - 60% of total volume, depending on the composition and density of the two phases.

6.3.3 Drop-size and Settling Time Measurements

The mixture transferred to the "photographic" cylinder was mixed at a predetermined speed. After hydrodynamic equilibrium was reached (more than 10 minutes), two or three photographs were taken. The stirrer was switched-off and the settling time to obtain the primary break was measured. This procedure was repeated for each mixture at four different speeds.

With mixtures containing high phosphoric acid concentrations, it was normally difficult to measure the drop-size even at the lowest possible mixing speeds, because the drops were very small due to the diminishing value of the interfacial tension. Therefore only settling time was measured for those mixtures.

6.4 MATERIALS USED

The process materials used in this work are presented in Table 6.1.

TABLE 6.1 Materials used and their specifications

No.	Material	Formula	Mol.wt.	density at 20°C	Refractive index at 20°C	minimum assay	Max.limit of impurities Non volatile %	Others %	Mfg Co.
1	Pentanol (n-amyl alcohol)	$CH_3.(CH_2)_4.OH$	88.15	0.814			0.01		H/W
2	tri-n-butyl orthophosphate	$[CH_3.(CH_2)_3]_3PO_4$	266.32	0.975	1.423-1.425		0.01	0.02	H/W
3	Di-isopropyl ether	$[(CH_3)_2CH]_2O$	102.18	0.725	1.367-1.369	98.0			BDH
4	4 methyl pentan-2-one (isobutyl methyl ketone)	$(CH_3)_2CH.CH_2.CO.CH_3$	100.16	0.809		97.5	0.01		H/W
5	Distilled water	H_2O	18.00	0.998					
6	Aluminium phosphate	$AlPO_4 + H_2O$	121.95	2.566			chloride(Cl) 0.01 sulphur(SO_4) 0.05 Iron (Fe) 0.01		BDH
7	Ferric ortho-phosphate	$FePO_4 + H_2O$	186.85	2.74					BDH
8	Calcium ortho-phosphate	$Ca_3(PO_4)_2$	310.18	3.14		90% $Ca_3(PO_4)_2$	Cl 0.5% sulphate(SO_4) 0.5% Iron(Fe) 0.5%		BDH
9	Magnesium phosphate	$Mg_3(PO_4)_2.6H_2O$	370.96						H/W
10	Ortho phosphoric acid	H_3PO_4 88% by weight.	98	1.75		88%			BDH

6.5 CLEANING PROCEDURE

All cylinders and bottles used were carefully and thoroughly cleaned after each run. The measuring cylinders used for binodal curve determinations were washed three times with hot tap water, then rinsed with distilled water twice and dried in an oven for quick re-use. The jacketted cylinders were first washed with hot tap water, then filled with distilled water with the heating water in the jacket flowing at 60°C. The agitators were switched on and the cleaning process continued for at least one hour. The distilled water was then replaced and further agitated. The water was then drained and the cylinders left to dry. The sampling bottles were cleaned in the same way as the measuring cylinders.

No necessity was found for the use of detergents except in very few cases such as when wet-process phosphoric acid was used. The use of detergents was avoided especially in the jacketted cylinders because of their effect (17) on the surface properties of dispersions.

6.6 ANALYSIS

6.6.1 Chemical Analysis

This included the determination of H_3PO_4 and cationic impurities in the extract and aqueous phases and measurements of specific gravity, viscosity, interfacial tension and solvent stability.

6.6.1.1 H_3PO_4 Concentration Determination

Phosphoric acid concentration in the various acid solutions was determined by pH titration. This method is very reliable, rapid, accurate, reproducible and requires no sophisticated equipment (179).

Huhti and Gartaganis (177) studied the composition of concentrated phosphoric acid solutions containing 68.8 - 86.3% P_2O_5 using filter paper chromotography. They found that as the mole ratio of water to P_2O_5 decreases the number of component acids increases. The relative proportion of these components were established to be a function of the overall P_2O_5 concentration only and not of the method of preparation. When the concentration of phosphoric acid was less than 68.8% P_2O_5 (95% H_3PO_4) only orthophosphoric acid was present. Acids with higher P_2O_5 concentrations would contain pyro, tri, tetra .... etc phosphate acid components. Accordingly, the solutions dealt with in this work were expected to contain only orthophosphate.

Orthophosphoric acid is a single molecular unit and contains one strong-acid function (hydrogen) and two weak-acid functions. Only one of the weak-acid hydrogens is strong enough to be detected using pH titration.

A titration curve for orthophosphoric acid is shown in Figure (6.4). The dissociation constants of orthophosphoric acid ($k_1 = 7.107 \times 10^{-3}$, $k_2 = 7.9884 \times 10^{-8}$ and $k_3 = 4.8 \times 10^{-13}$ at $25^{\circ}C$ (178)) are such that the pH titration curve has inflection

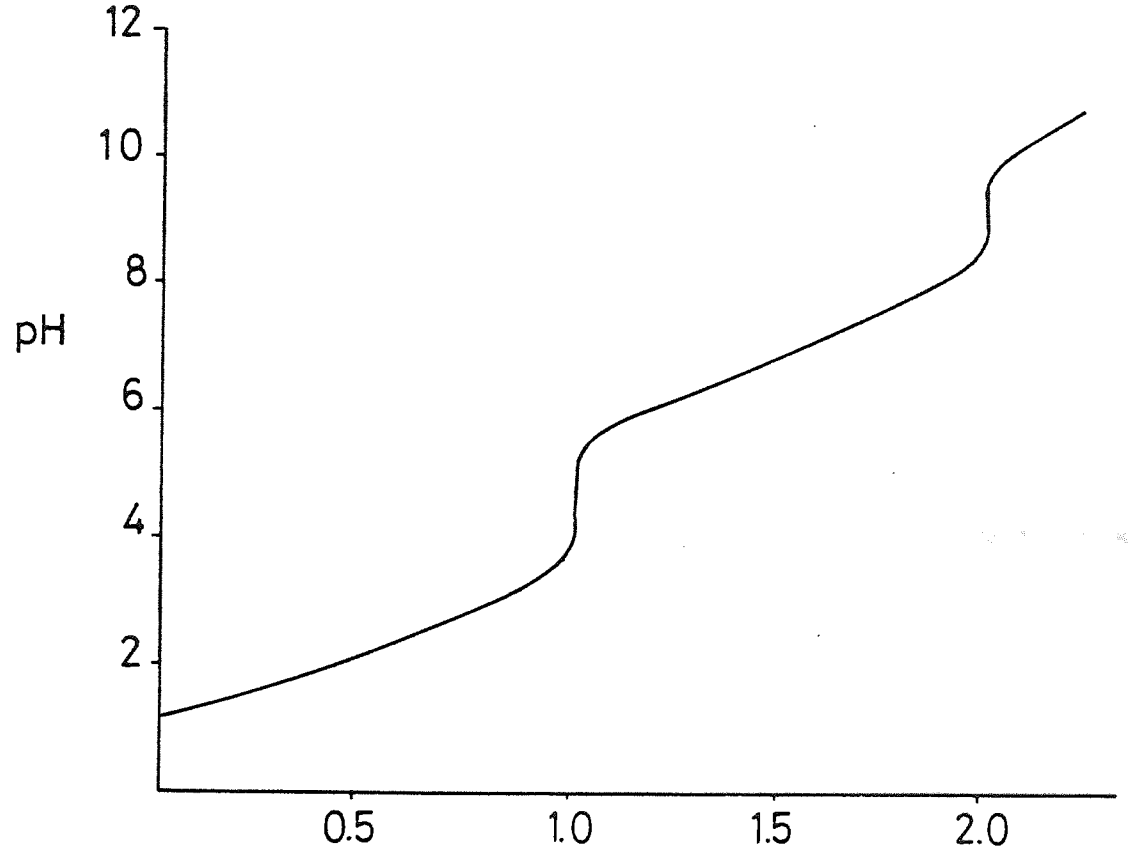


Fig. 6.4 Titration curve for orthophosphoric acid

points near pH 4.5 and 9 (179). The amount of alkali required to titrate a phosphate solution from its original pH to a pH 4.5 end point is a measure of its strong-acid function. Titration from the end point at 4.5 to the end point at pH 9 measures the weak acid function.

The amount of alkali required to reach these two end points was always the same for a given sample, except in the case of an aqueous phase (raffinate) containing calcium or magnesium phosphate impurities. In these cases the amount of alkali required for the second titration was always about 0.5 - 3% higher than that for the first titration. This was explained due to the interference of these impurities with the strong acid hydrogen. Further investigation confirmed this and results and conclusions are presented in Appendix (III).

The strong and weak acid titrations can be represented by the following equations using NaOH as the alkali:

$$NaOH + H_3PO_4 \rightarrow NaH_2PO_4 + H_2O$$

$$NaOH + Na\ H_2PO_4 \rightarrow Na_2HPO_4 + H_2O$$

Procedure

Two samples of each phase were weighed accurately in amounts equivalent to 20 - 50 ml of 0.1N NaOH for each end point. The equipment for titration is shown in Figure 6.5 and is composed of the following: -

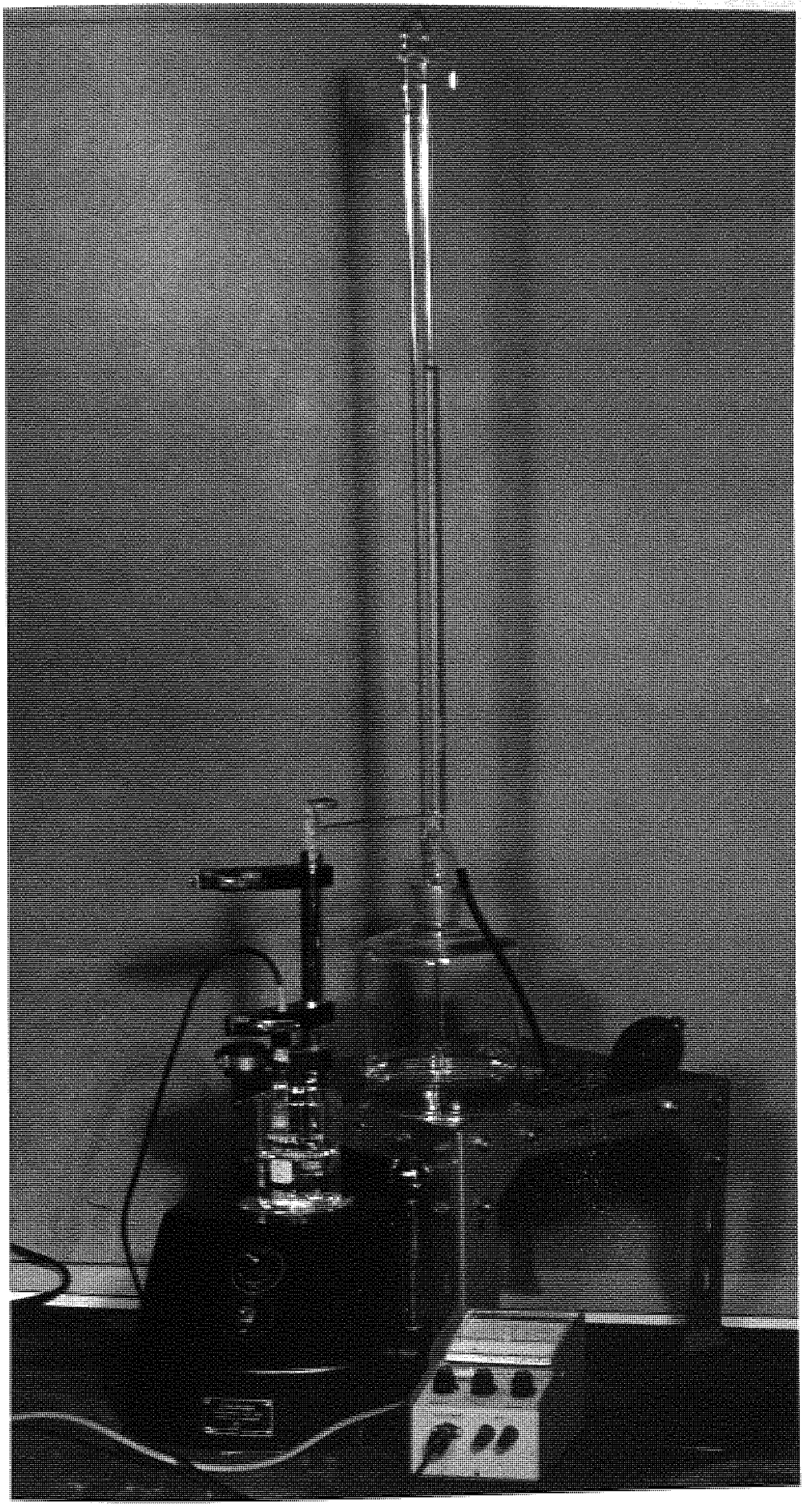


Fig. 6.5. pH titration equipment

1. Automatic, 50ml burette, with a 2 litre NaOH reservoir.
2. pH meter.
3. Magnetic stirrer.
4. 400ml titration beaker and a PTFE coated stirring magnet.
5. Buffer solutions.

The two samples of each phase were titrated for their strong and weak acid functions. When the deviation between the two samples was higher than 0.3% a third sample was tested and the average of the best two samples within the accuracy required was taken.

There was no difficulty in measuring the H_3PO_4 concentration in solvent rich (extract) samples, because the samples were always diluted in large amounts (50 - 100ml) of distilled water, which extracts the H_3PO_4 completely from the solvent.

6.6.1.2 Determination of Impurity Concentration

Both atomic absorption and flame emission were used, when ever possible, for the measurement of Al, Fe, Ca and Mg in both aqueous and solvent phases. These methods are gaining popularity for being rapid, reliable, accurate and able to detect very small amounts of elements (179).

In atomic absorption analysis, a solution of the sample was sprayed into a flame which dried, volatilized and broke the sample into clouds of neutral atoms. Light from a hollow cathode lamp passed through the flame and the netural atoms of the

sample. The intensity of this light was decreased due to some absorption by the neutral atoms. The amount of light absorbed is a function of three factors -

(i) Absorbtivity constant for the element at the wavelength measured.

(ii) Length of the light path through the flame.

(iii) Concentration of the element being measured, taken as a direct relative measure of the number of neutral atoms.

By making the first two factors constant, the amount of light absorbed is a measure of the concentration of the element.

In addition to neutral atoms other species may absorb light in the flame. Ionic species may also absorb their respective lines, however, the ratio of the ionic species to the neutral is so small that at the temperature used neutral atoms are primarily measured (180).

Flame emission, like atomic absorption, used a flame to disperse the sample and produce a cloud of atoms. However, instead of a light source, emission analysis used the flame itself as an energy source to excite the ground state neutral atoms. When the excited atoms returned to ground state, the energy acquired from the flame was released, partly in the form of light of wavelength characteristic of the emitting species. The intensity of this emitted light is directly proportional to the concentration of that atom in the flame.

With some elements (Al, Fe and Ca included), either atomic absorption (AA) or flame emission (FE) can be used with essentially equal accuracy and precision (180). Other elements are better analysed by one of these techniques than the other depending on the absorbance and excitation nature of the element. Magnesium is better analysed by atomic absorption. In general, flame emission may be less specific than atomic absorption and is subject to greater spectral interferences.

The equipment used was an IL 151 which can perform both analysis techniques separately. Figure 6.6 shows the equipment connections. A nitrous oxide-acetylene flame, burning at a temperature near 3000^{o}C was used throughout to break the element - PO_4 bonding and produce enough neutral and excited atom population.

The samples were weighed and diluted to lie within the recommended concentration region. With AA these were up to 90ppm for Al, up to 10ppm for Fe and Ca, and up to 1ppm for Mg samples. The operating procedure of the specific equipment IL 151 was followed and is given in (180).

6.6.1.3 Determination of Physical Properties

(i) Interfacial Tension.

Interfacial tension was determined using the standard du Noüy method on a 'White' torsion balance. The samples were placed in a bath operating at 25^{o}C for at least two hours.

(ii) Specific Gravity.

Specific gravity was measured using specific gravity bottles. The samples were stored in a bath operating at 25°C for at least two hours prior to measurements.

(iii) Viscosity.

Viscosity was measured using a Cannon-Fensky U tube Viscometer, i.e. by timing the passage of the fluid through a capilliary immersed in a constant temperature bath (25°C).

6.6.1.4 Solvent Stability

This was determined by analysing solvent containing samples periodically using a Gas Liquid Chromotography (with a katherometer detector).

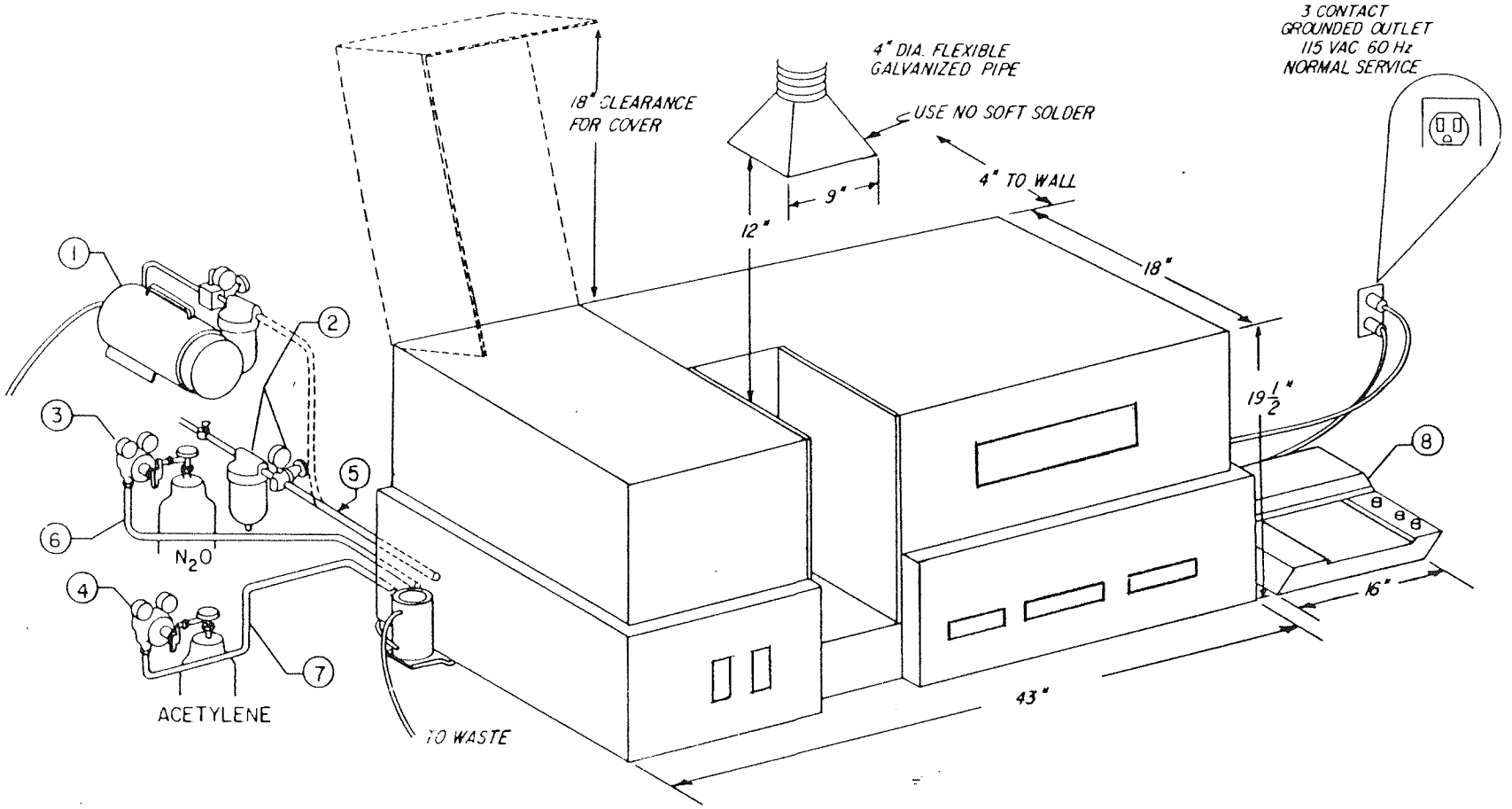
Attempts were made to find out whether the solvent had partly decomposed or had changed to other organic chemicals, which would appear as a new (different) component in the chromotograph.

In Gas Liquid Chromotography, the components of a sample to be analysed are separated by making use of differences in their partition coefficient between the moving gaseous and stationary liquid phases. The liquid stationary phase is usually absorbed on an inert solid which acts as a support, and the two phases come into contact in a tube termed the "column". The stationary phase must be a liquid which is chemically stable over a fairly wide range of temperature, inert, having low vapour

pressure and being a good solvent for the components. Small amounts of sample are injected into the column which is operating under controlled conditions. The analytical output is in the form of a chromotograph, the number of peaks on which is equal to the number of components desorbed by the carrier gas. The position of each chromotograph peak is representative of a certain component and its area to the concentration. The operating procedure for the particular equipment was followed and is given in (182).

6.6.2 Droplet Photographic Analysis

The photographs taken were enlarged to give a magnification factor of 4 over the real object. A typical photograph is reproduced as Figure 6.7. The photographic prints were analysed using a Carl Zeiss particle Size Analyser T.G.Z.3. Initially 300 - 350 droplets were counted from the two or three photographs taken for each event, subsequently it was observed that 200 - 250 droplets were quite enough for accuracy, because of the homogeneity of the dispersions.



(1) Air Compressor, Filter, Regulator Assembly (27071-01)

(2) Air Filter/Regulator Assembly (27457-01) (optional)

(3) Nitrous Oxide Pressure Regulator (51420)

(4) Acetylene Pressure Regulator (51431)

(5) Air Hose, Green, 10 ft. (24114)

(6) Nitrous Oxide Hose, Black, 10 ft. (24115)

(7) Acetylene Hose, Red, 10 ft. (24116)

(8) Strip Chart Recorder (60150)

Fig. 6.6 Atomic Absorption/Emission (IL 151) Connections

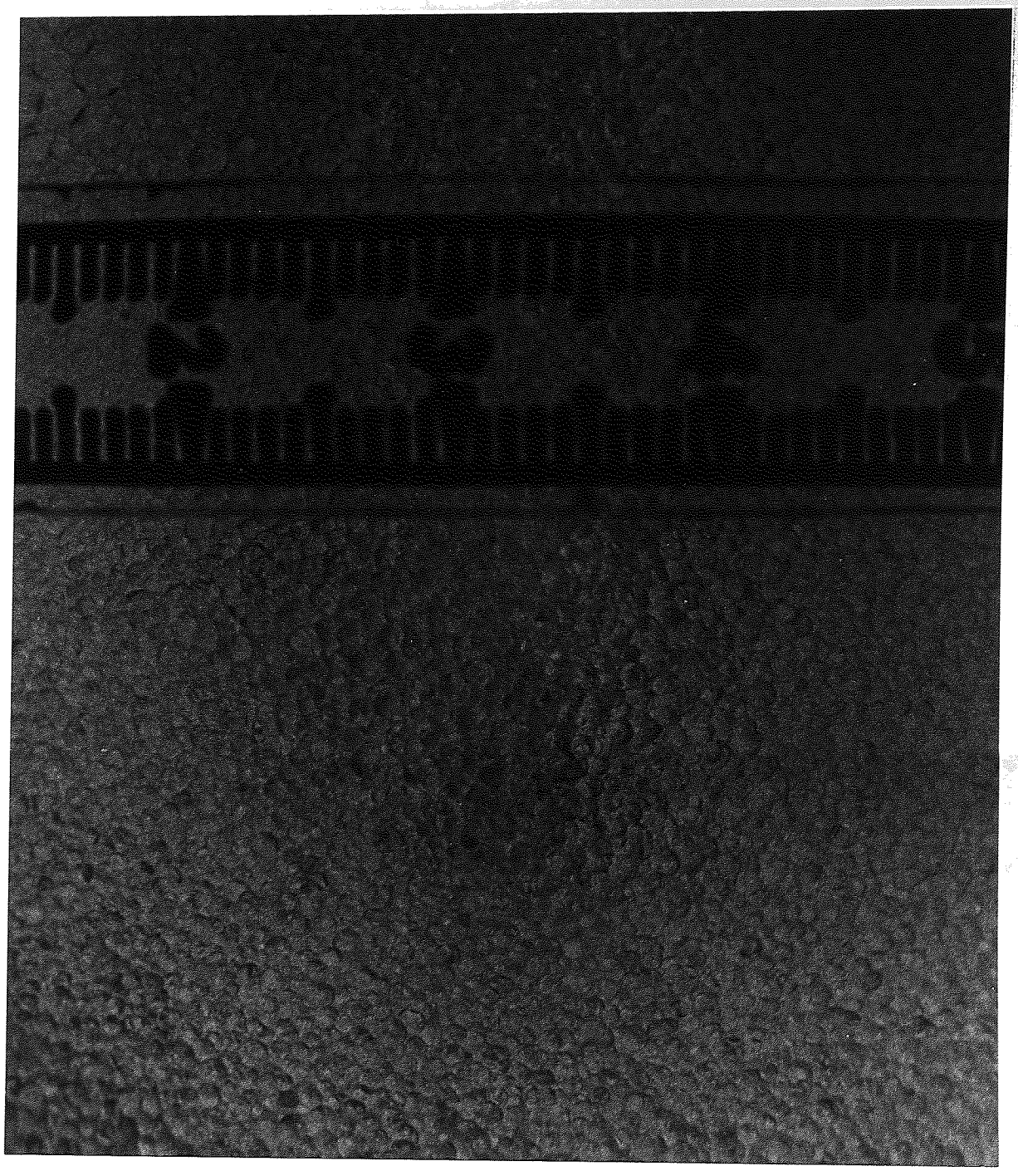


Fig.6.7 Sample of the photographs printed for drop-size measurements.

CHAPTER SEVEN

EXPERIMENTAL RESULTS

7.1 PHASE EQUILIBRIUM RESULTS

The phase equilibrium data for the four systems; n-amyl alcohol; tri-n-butyl phosphate; di-iso propyl ether; and methyl isobutyl ketone - with water and phosphoric acid using pure acid and acids containing a known amount of an impurity (Fe, Al, Ca or Mg) are presented in the form of ternary diagrams and distribution curves. Phosphoric acid and its impurities are solutes in the systems distributing between an aqueous phase and a solvent phase.

7.1.1 Effect of H_3PO_4 Concentration on its Distribution Coefficient

The distribution coefficient of phosphoric acid in all systems studied increased with an increase of acid concentration. With n-amyl alcohol and tri-n-butyl phosphate the increase was gradual (Figures 7.4, 7.8), while it was more likely to be a step change with di-iso propyl ether and methyl iso butyl ketone (Figures 7.12, 7.16). The concentration at which this change takes place is characteristic for each system.

7.1.2 Effect of Cation Impurities on the Distribution of Phosphoric Acid

The impurities present increased the size of the heterogeneous area of the phase equilibrium diagram of the systems studied. In other words the mutual solubility of the solvent and aqueous phases decreased and in particular the solubility of water in the solvent phase. The presence of impurities also decreased the solubility of phosphoric acid in the extract phase at any given H_3PO_4 concentration and therefore lowered the slope of the distribution curve of phosphoric acid. These effects are shown in the phase equilibrium diagrams and distribution curves for phosphoric acid in the presence of impurities (Figures 7.1 - 7.16). The binodal curve for all the systems with an impurity present was the same within less than $\pm$ 0.5%, so the average binodal curve was used.

The distribution coefficients of phosphoric acid in the presence of Ca or Mg appeared to be higher than those (at the same H_3PO_4 concentration) for Fe or Al. This is because of the slight decrease in the aqueous raffinate H_3PO_4 concentration due to chemical reactions of $Ca_3(PO_4)_2$ and $Mg_3(PO_4)_2$ with the acid as will be shown in Appendix (III).

7.1.3 Effect of Phosphoric Acid Concentration on the Distribution of Impurities

Only one metallic impurity was added at a time. It was found that the distribution coefficient of impurities in all systems studied increased with an increase in acid concentration

in the extract phase as shown in Figures 7.17 to 7.20. At any given H_3PO_4 concentration in the extract phase the distribution coefficient of impurities were generally in the order: ion (Fe^{3+}) > calcium > aluminium > magnesium. Comparison of the solvents showed that the distribution coefficient of impurities descended in the order: n-amyl alcohol > methyl iso butyl ketone > tri-n-butyl phosphate > di-iso propyl ether.

The extraction of a wet-process phosphoric acid in one stage and the purification of the resulting extract by contacting it with a pure aqueous phase having the same H_3PO_4 concentration as the initial impure raffinate is shown in Figures 7.22 to 7.25. It was observed that the distribution coefficient of an impurity was generally higher when wet-process acid was used instead of prepared impure acid for any given system and H_3PO_4 concentration. The Figures 7.22 to 7.25 show that the distribution coefficient of all impurities in any of the systems was generally higher in the purification stage than in the extraction stage. This was first thought to be because the distribution coefficient increases at low impurity concentration. However, the concentration of H_3PO_4 in the extract phase also increased during the purification stage. This happened although the aqueous and solvent phases were thought to be at equilibrium with respect to H_3PO_4. This phenomenon can be explained by the contraction of the binodal curve at lower impurity concentrations resulting in higher H_3PO_4 concentration as described earlier. The increase in H_3PO_4 concentration in the extract phase would certainly increase the

distribution coefficient of the impurities as shown in Figures 7.17 - 7.21. Therefore the concentration level of an impurity might not be the reason for the change in its distribution coefficient.

The effect of impurities on the tri-n-butyl phosphate system was less significant than for the other solvent systems both on the binodal curve and the tie lie concentrations.

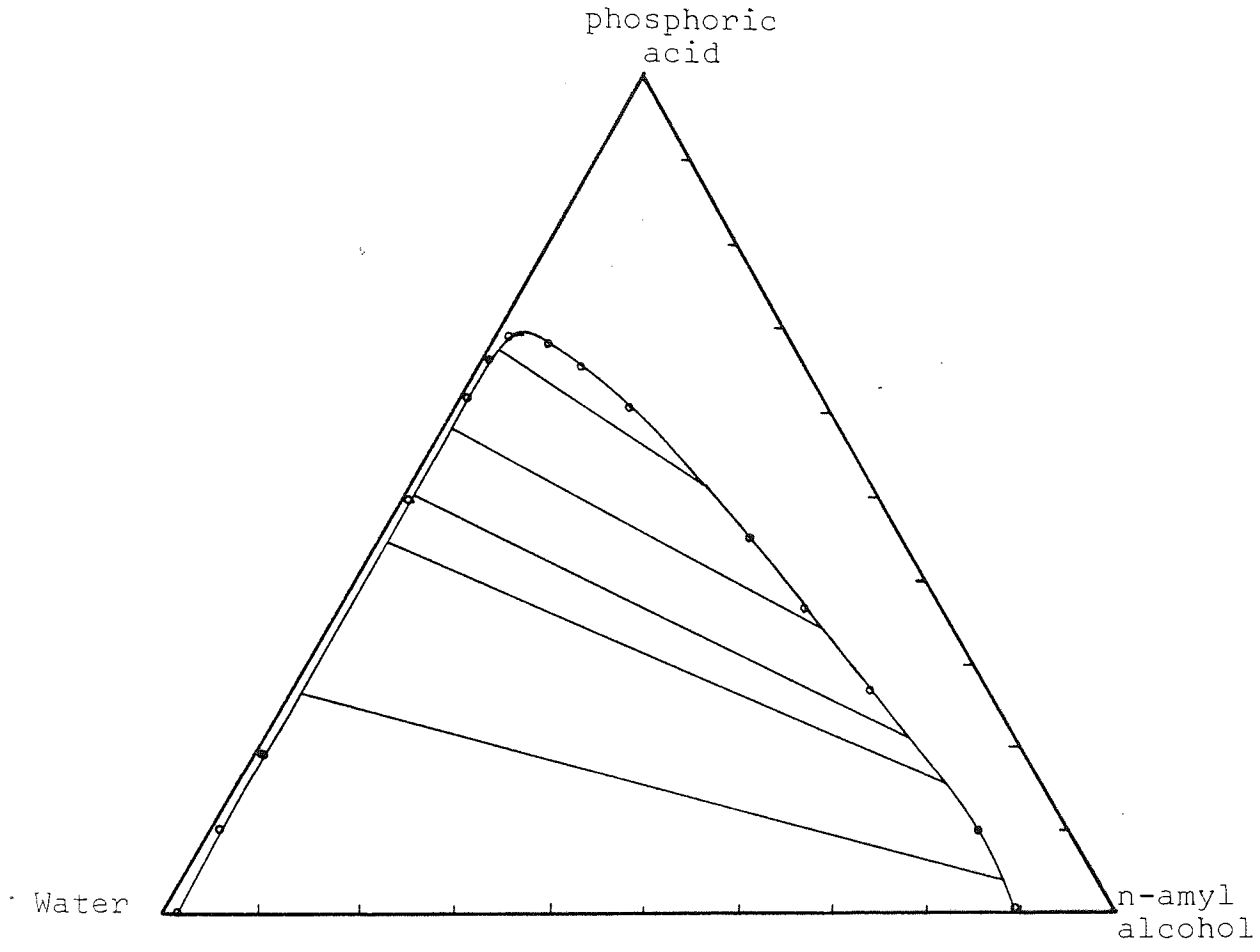


Fig. 7.1 Ternary phase equilibrium - diagram at 25°C
for water - phosphoric acid - n-amyl alcohol

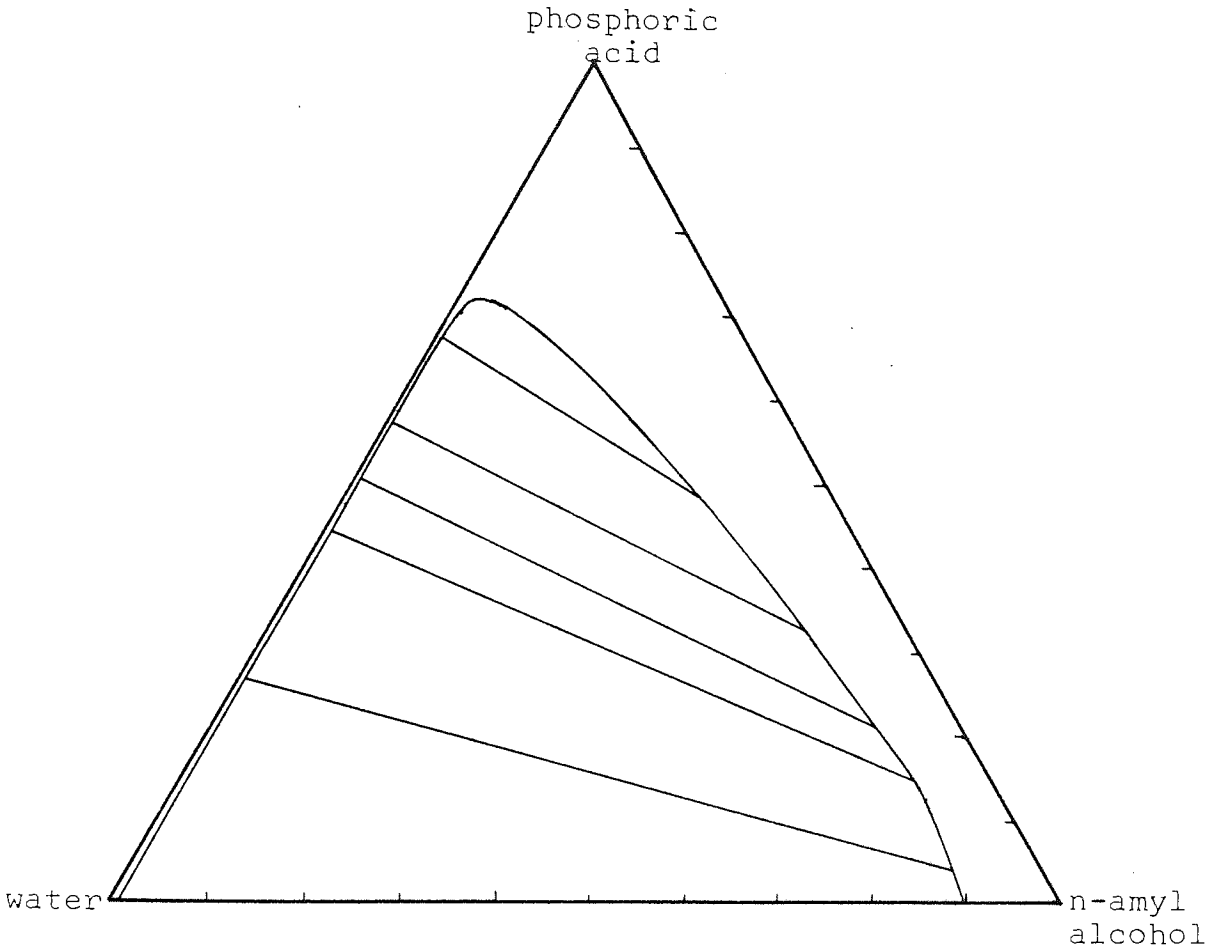


Fig. 7.2 Ternary phase equilibrium diagram at 25°C for water - phosphoric acid - n-amyl alcohol in presence of 0.5% Fe, Ca, Mg or 0.3% Al in the aqueous phase.

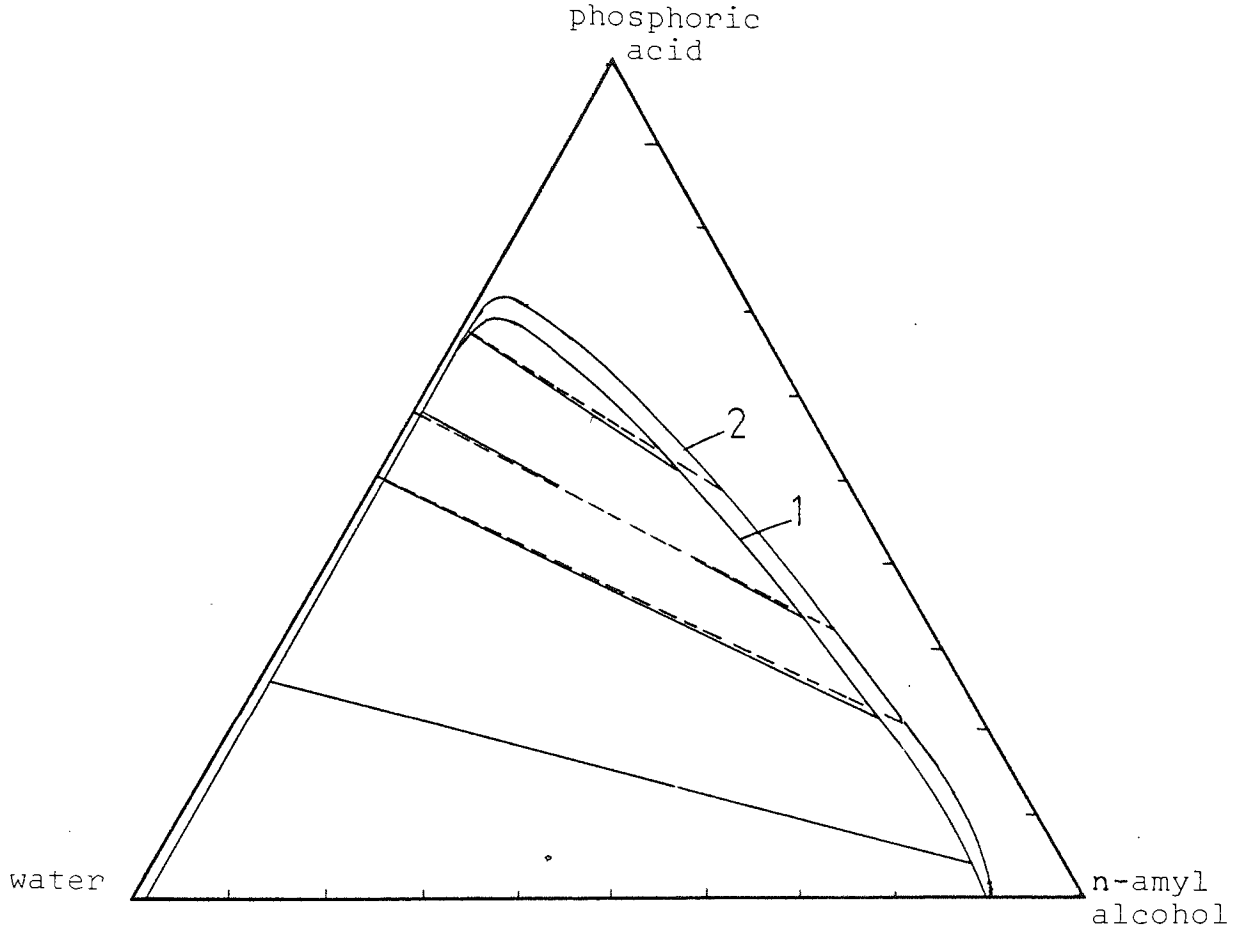


Fig.7.3 Comparison between ternary phase equilibrium diagrams at 25°C of water - phosphoric acid - n-amyl alcohol 1) for pure system
2) for impure system

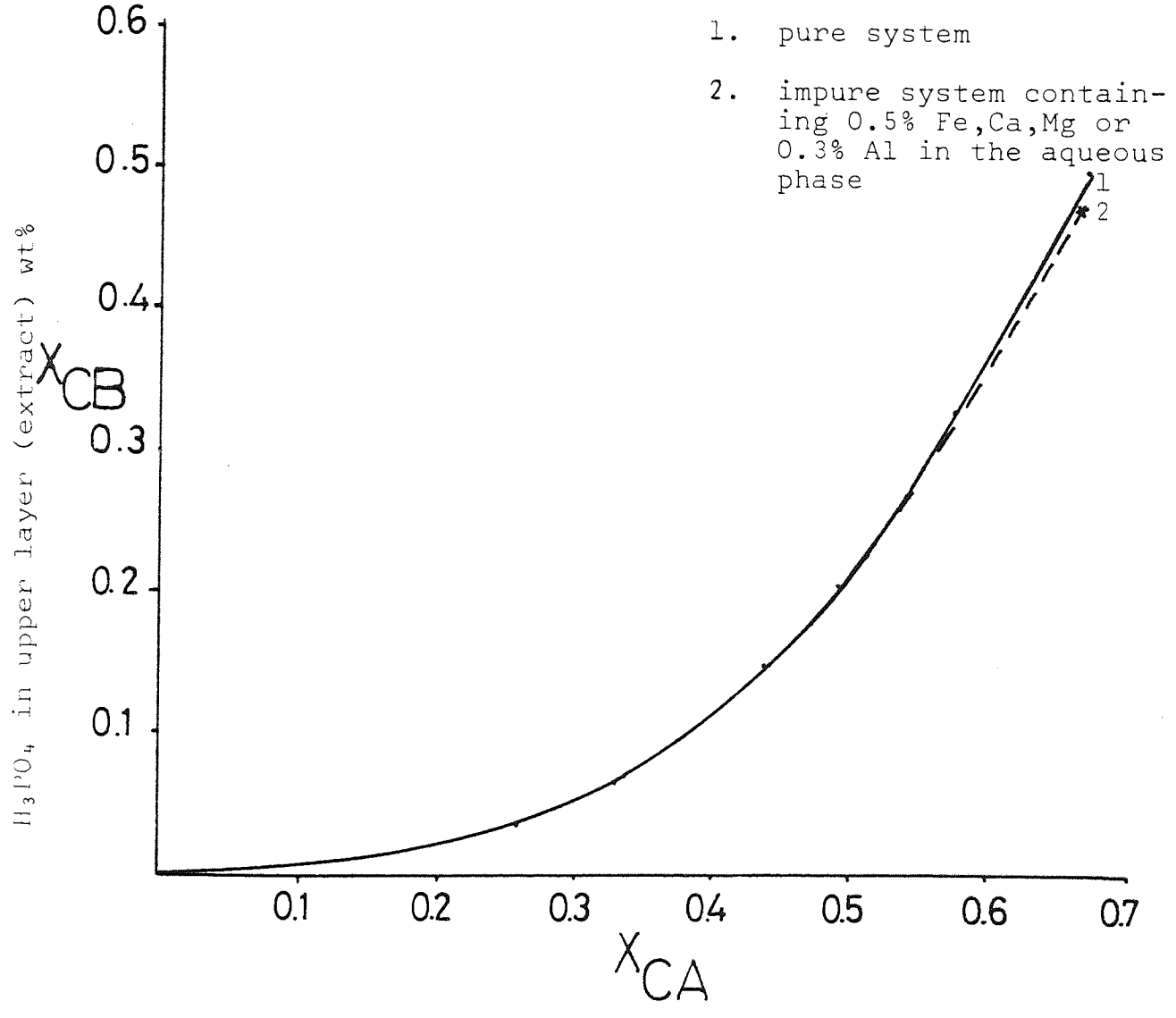


Fig.7.4 Distribution curve for phosphoric acid in the sytem water - phosphoric acid - n-amyl alochol at 25°C

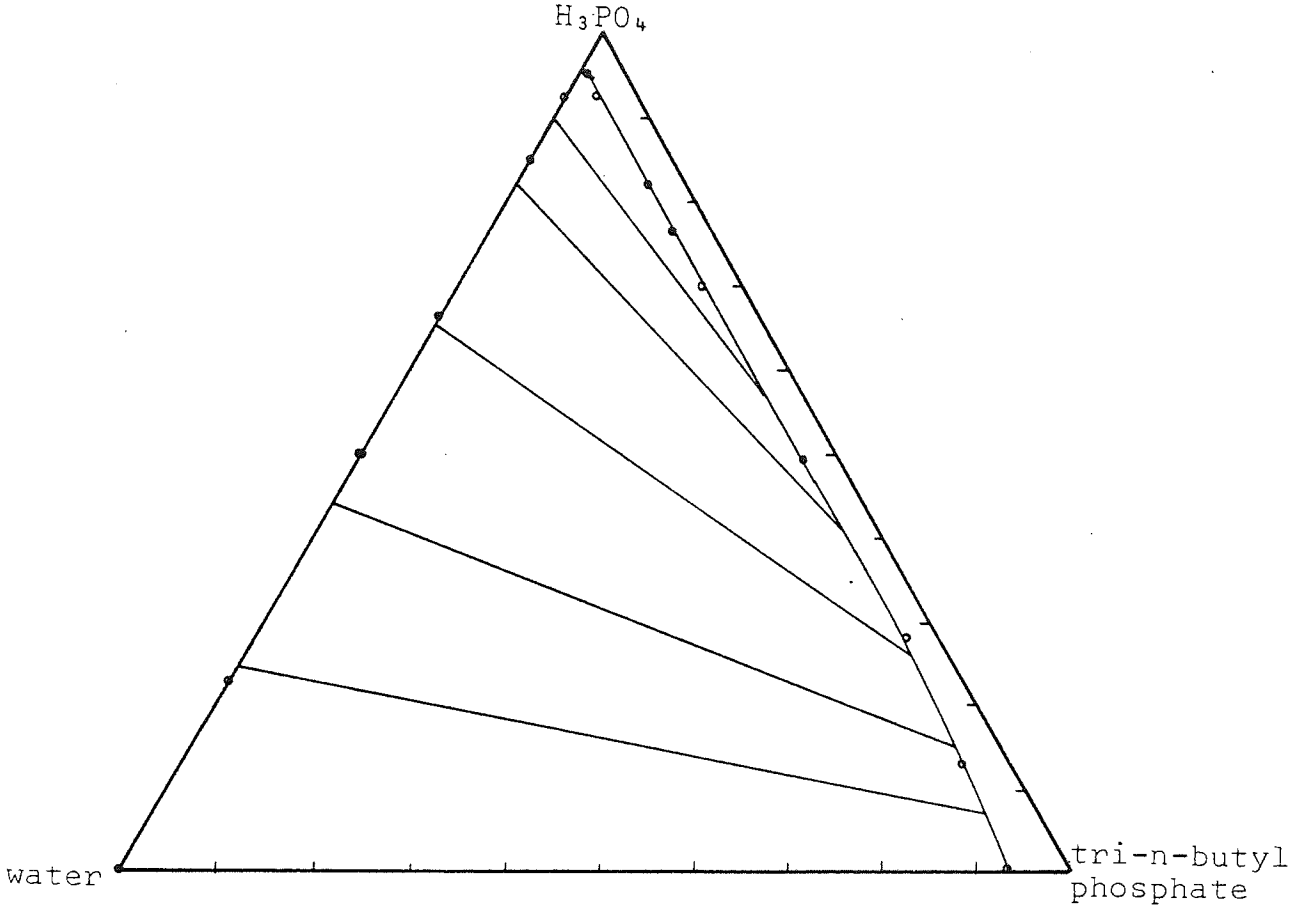


Fig.7.5 Ternary phase equilibrium diagram at 25°C for water - phosphoric acid - tri-n-butyl phosphate.

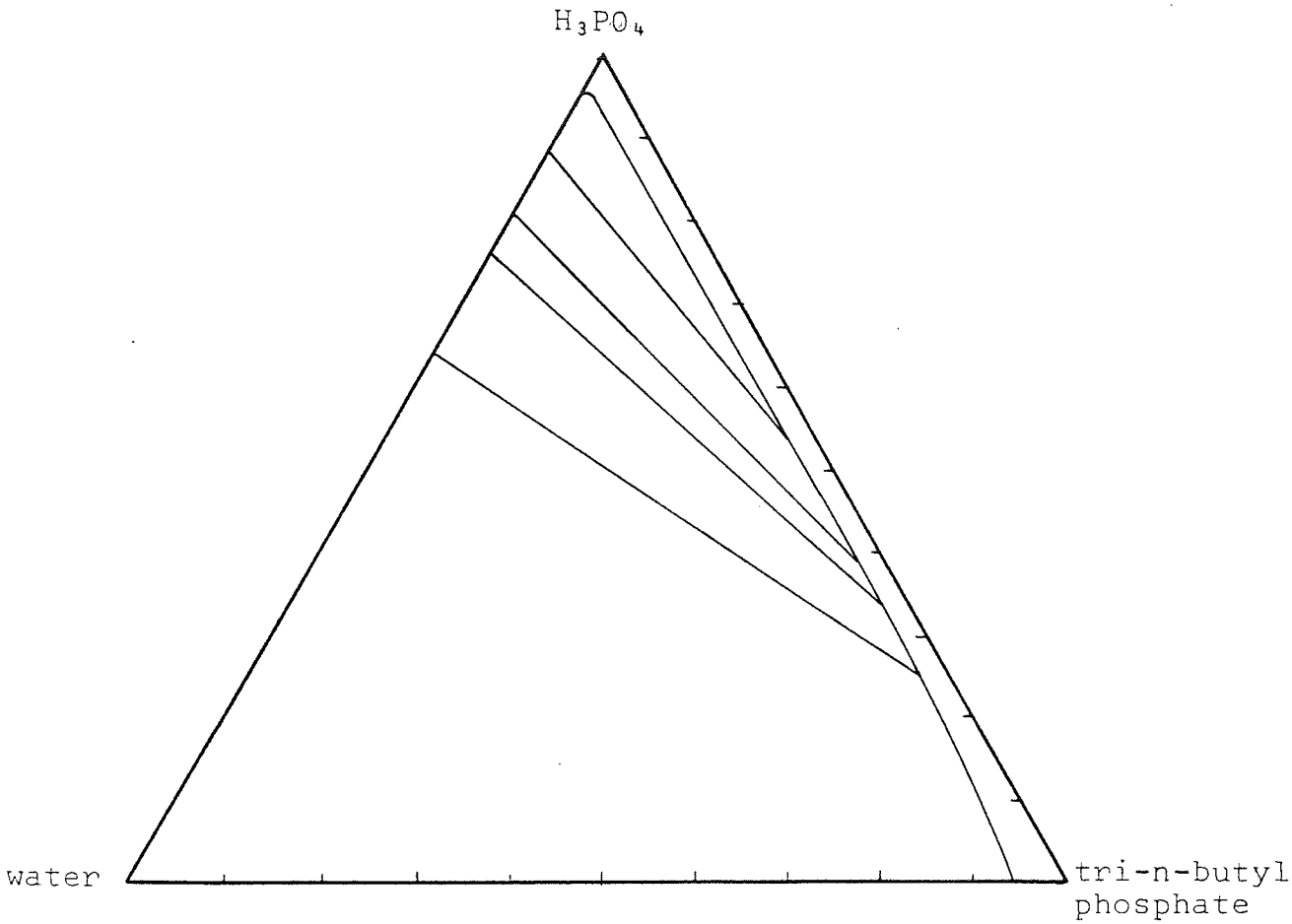


Fig.7.6 Ternary phase equilibrium diagram at 25°C for water - phosphoric acid - tri-n-butyl phosphate in presence of 0.5% Fe,Ca,Mg or 0.3% Al in the aqueous phase.

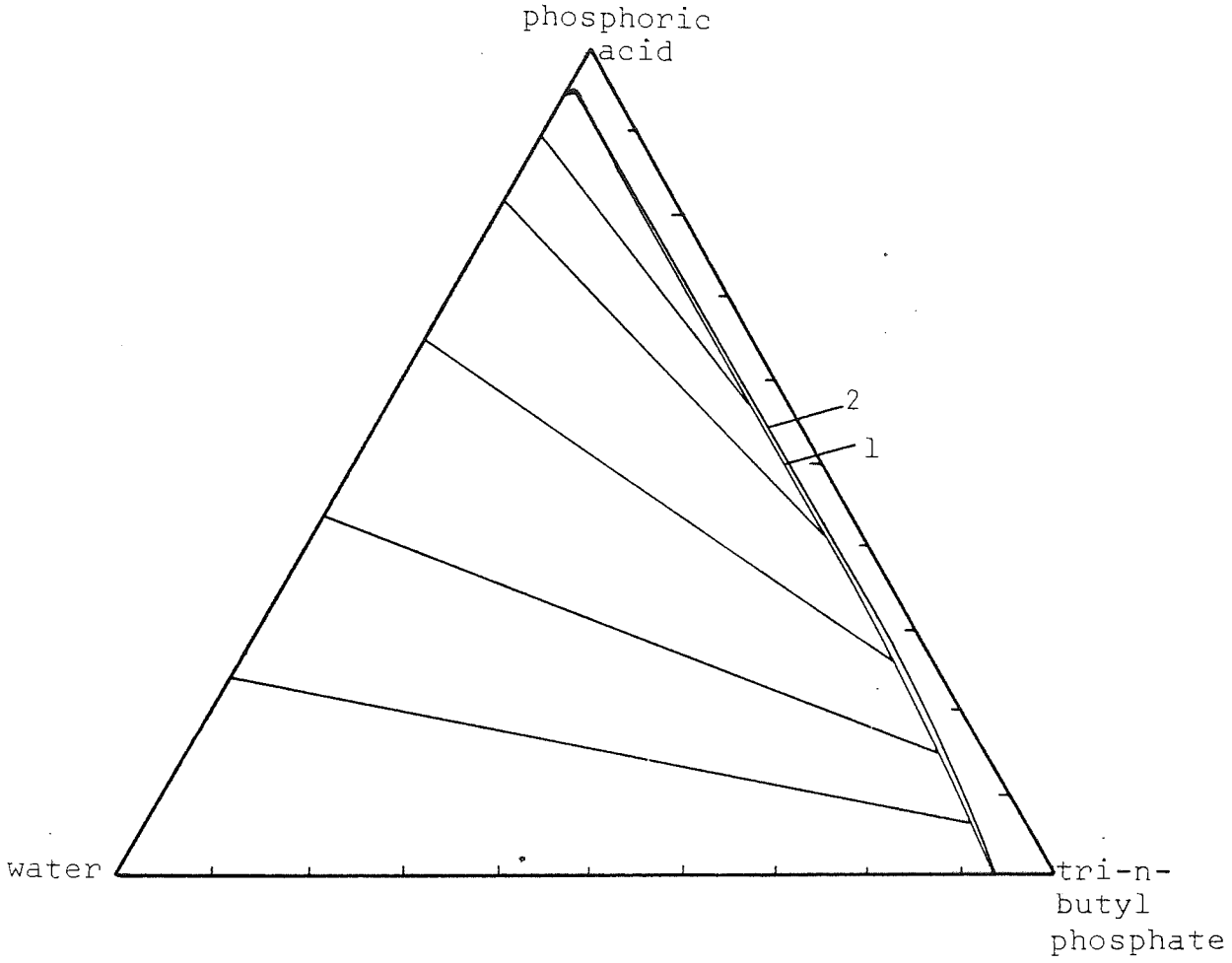


Fig.7.7 Comparison between ternary phase equilibrium diagrams at 25°C

1. for pure system
2. for impure system

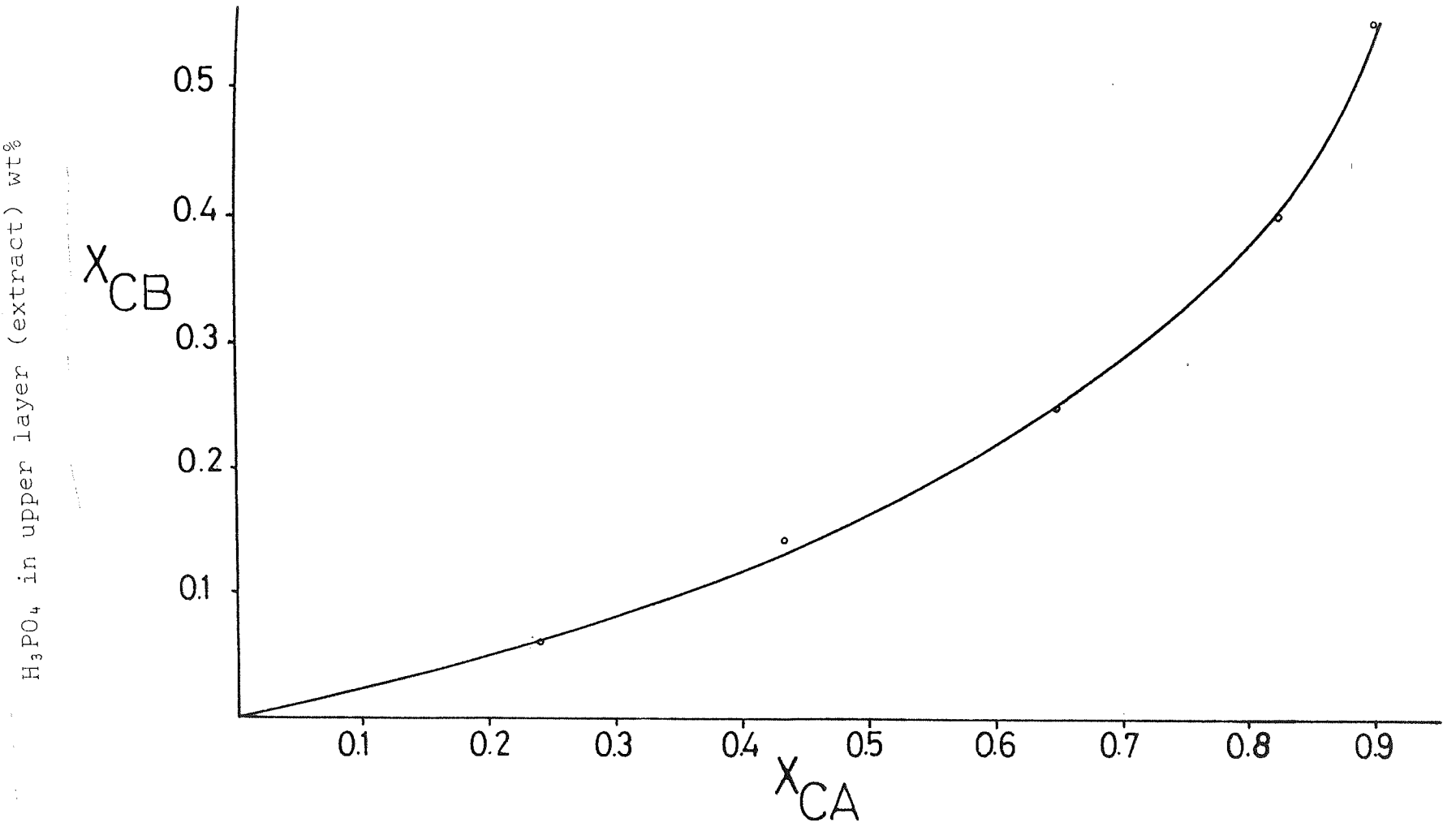


Fig.7.8 Distribution curve for phosphoric acid in the system water - phosphoric acid - tri-n-butyl phosphate at 25°C

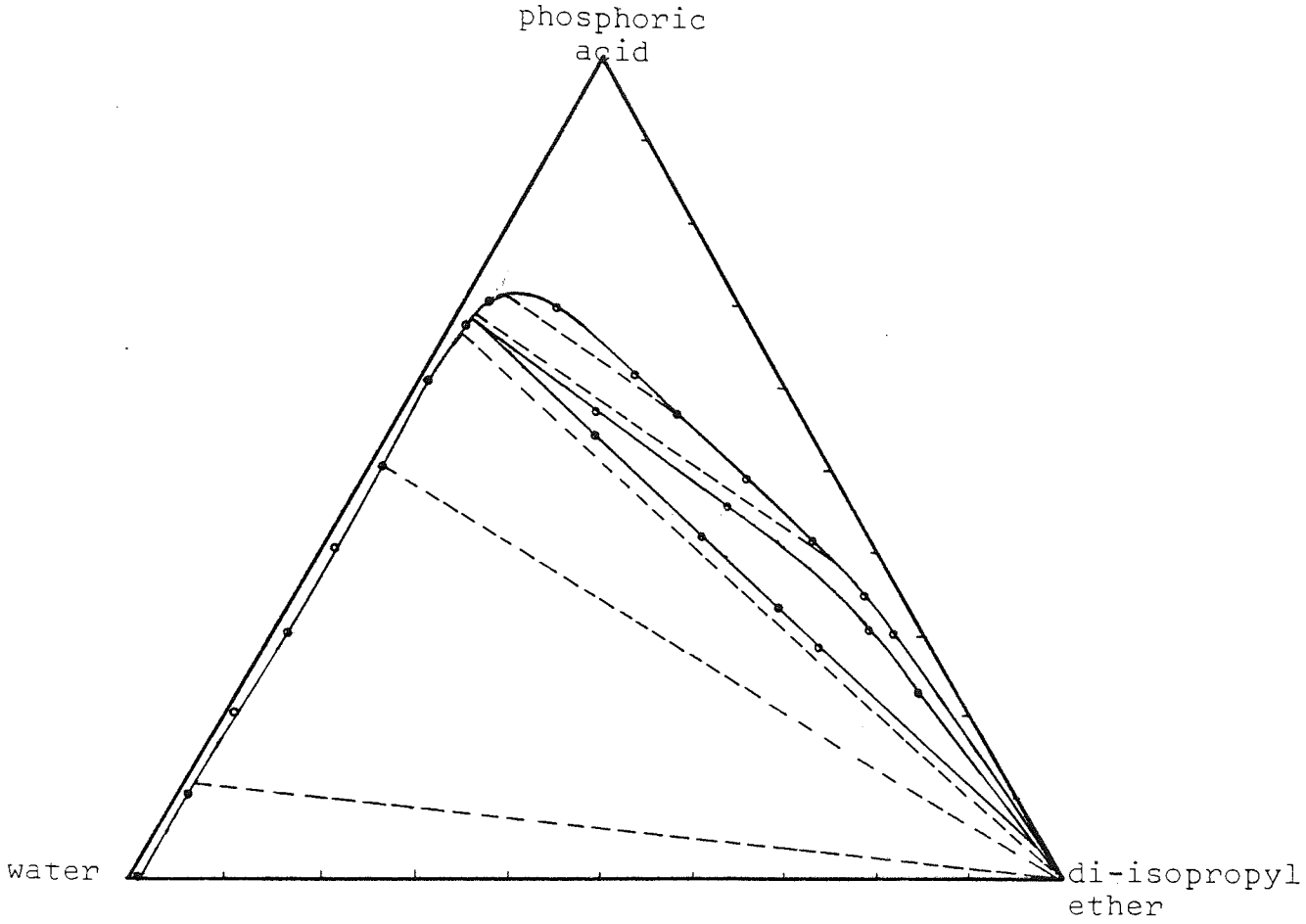


Fig.7.9 Ternary phase equilibrium diagram at 25°C for water - phosphoric acid - di-isopropyl ether

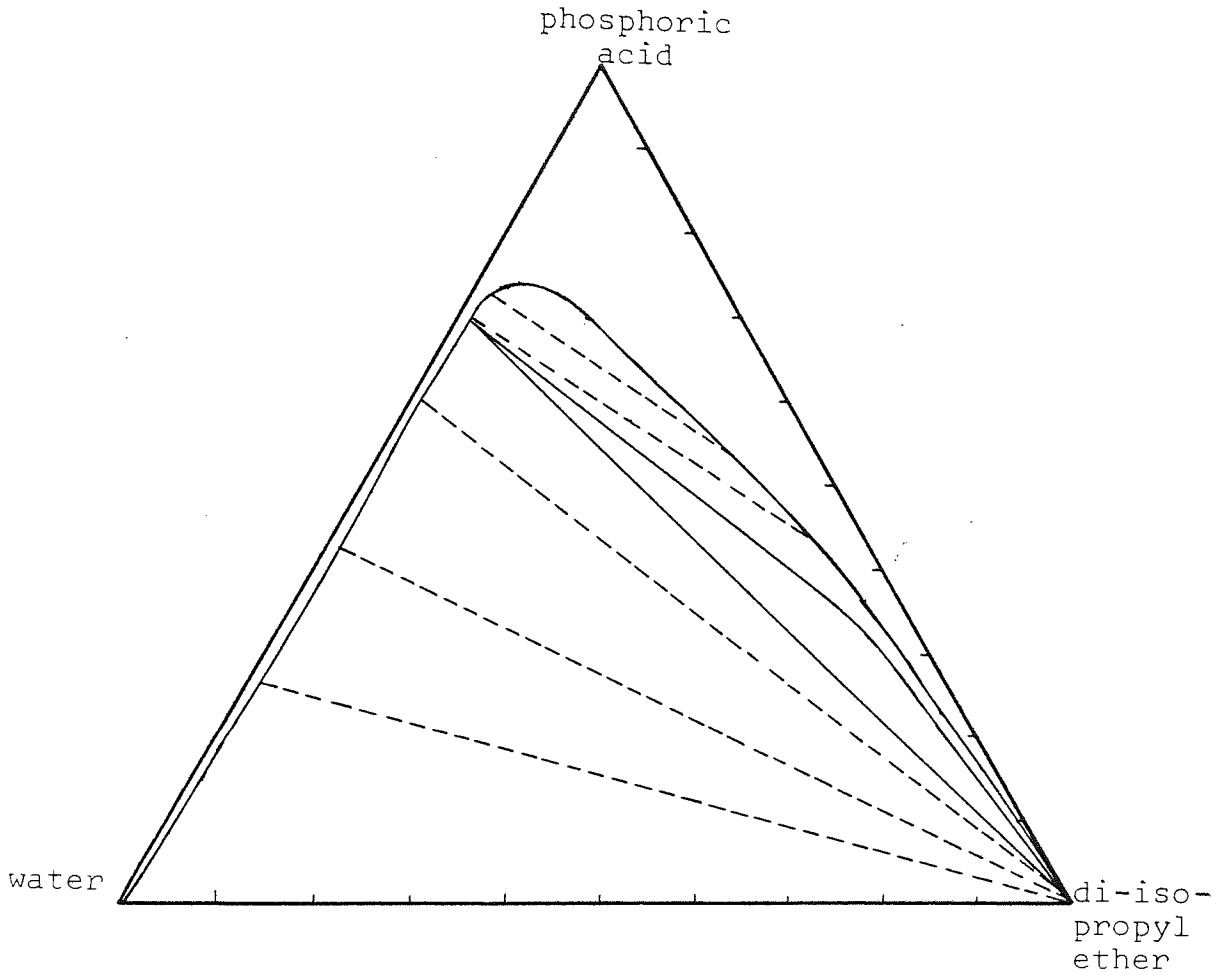


Fig.7.10 Ternary phase equilibrium diagram at 25°C for water - phosphoric acid - di-isopropyl ether in presence of 0.5% Fe,Al,Mg or 0.3% Al in the aqueous phase

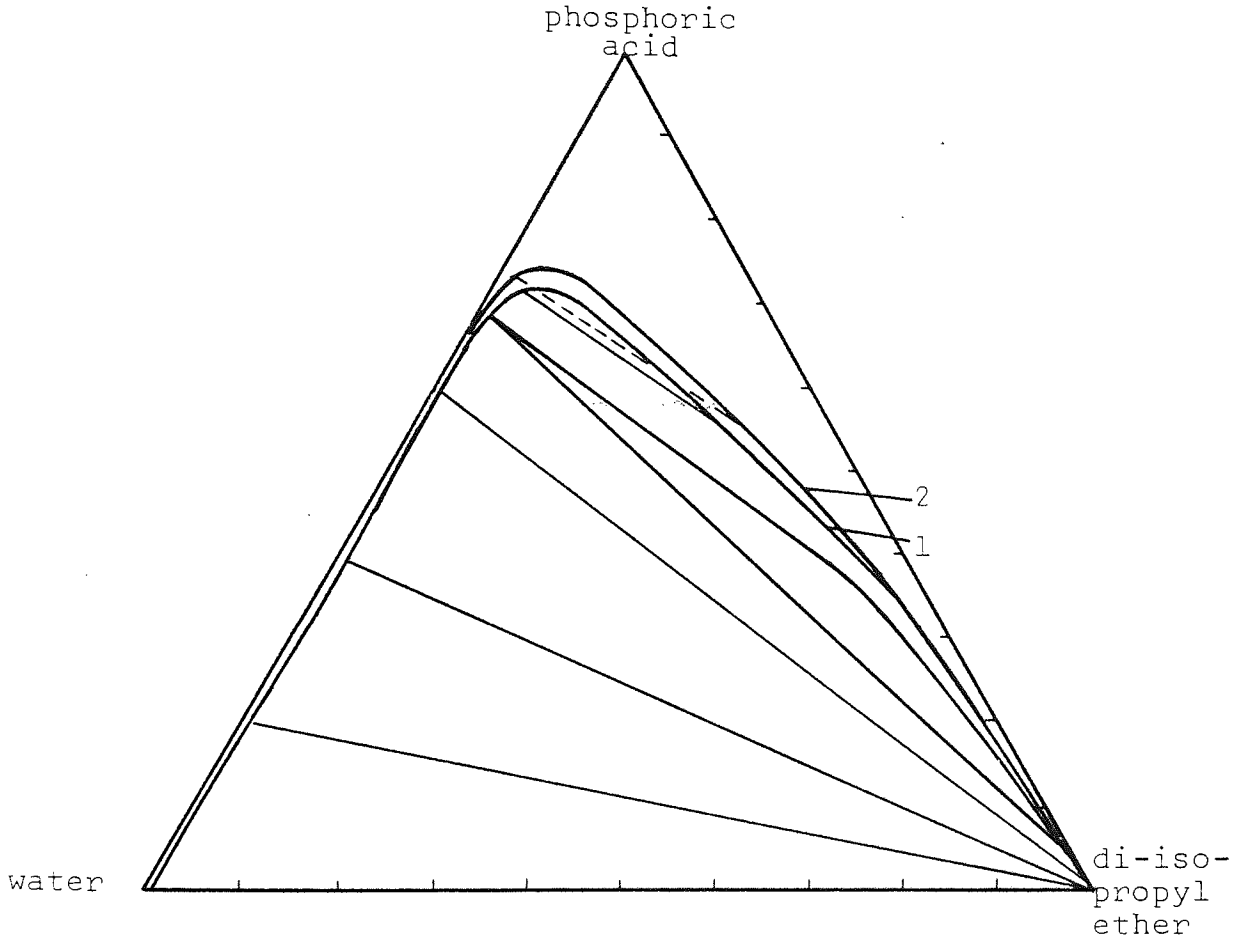


Fig.7.11 Comparison between phase equilibrium diagrams at 25°C

1. for pure system
2. for impure system

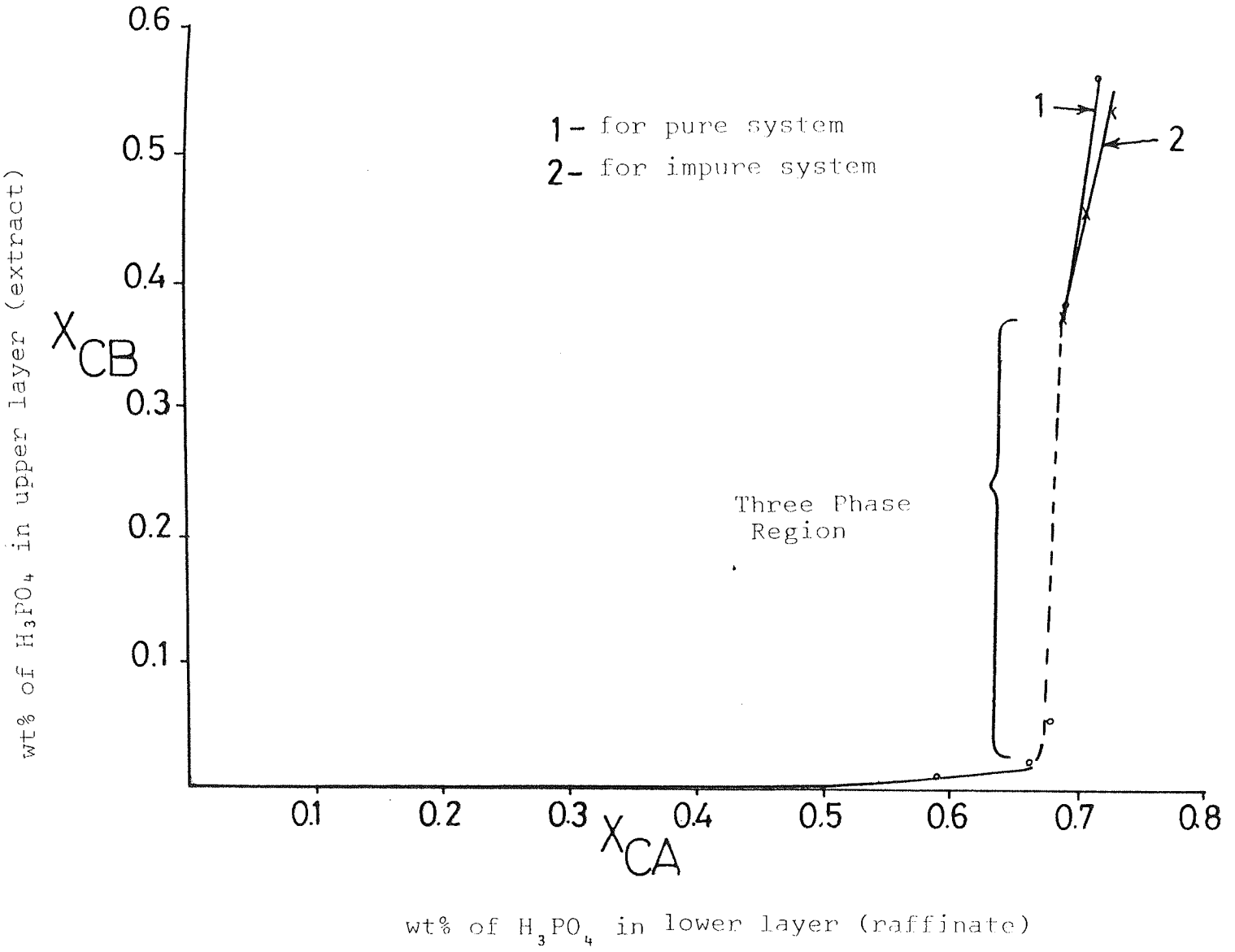


Fig. 7.12 Distribution curve for phosphoric acid in the system water - phosphoric acid - di-isopropyl ether at 25°C.

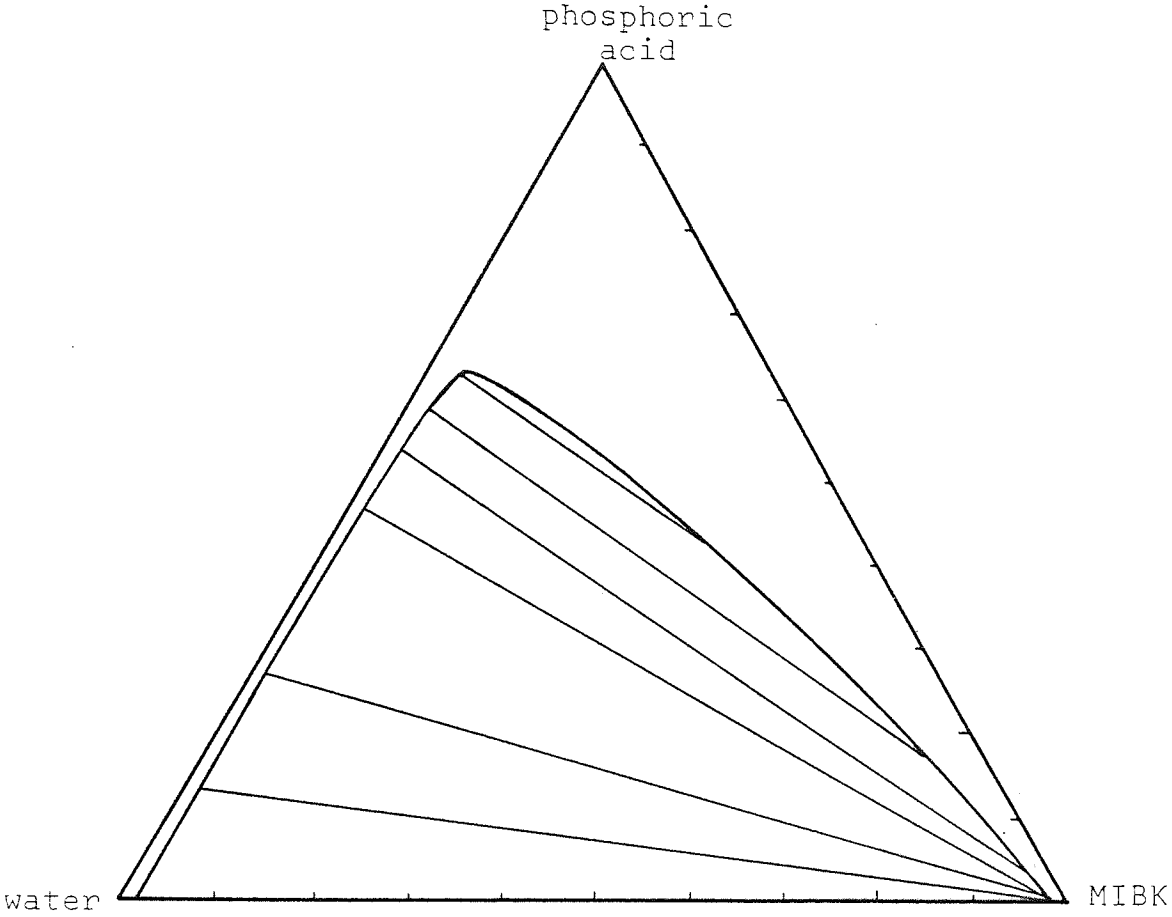


Fig. 7.13 Ternary phase equilibrium diagram at 25°C for water - phosphoric acid - methyl-isobutyl ketone

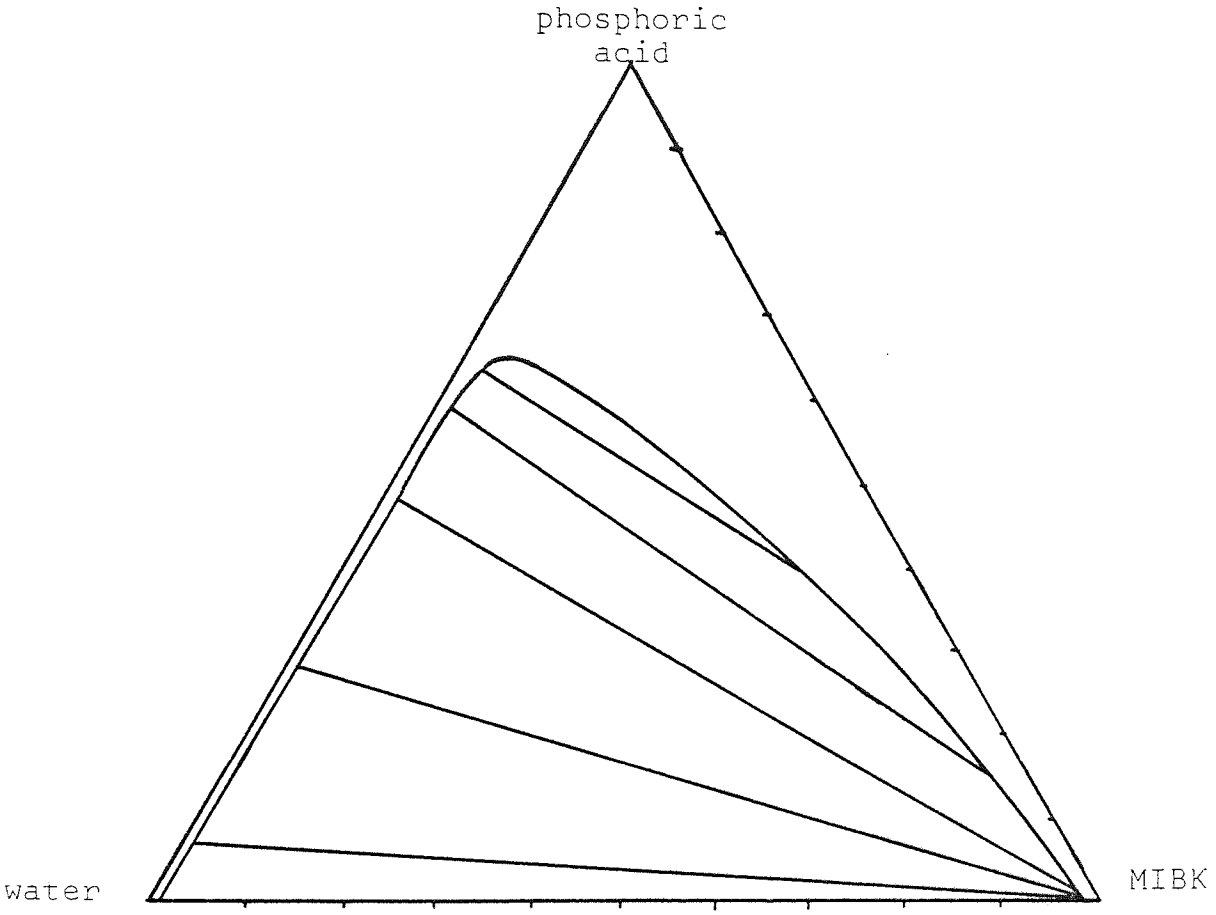


Fig.7.14 Ternary phase equilibrium diagram at 25°C for water - phosphoric acid - methyl isobutyl ketone in presence of 0.5% Fe,Ca,Mg or 0.3% Al in the aqueous phase

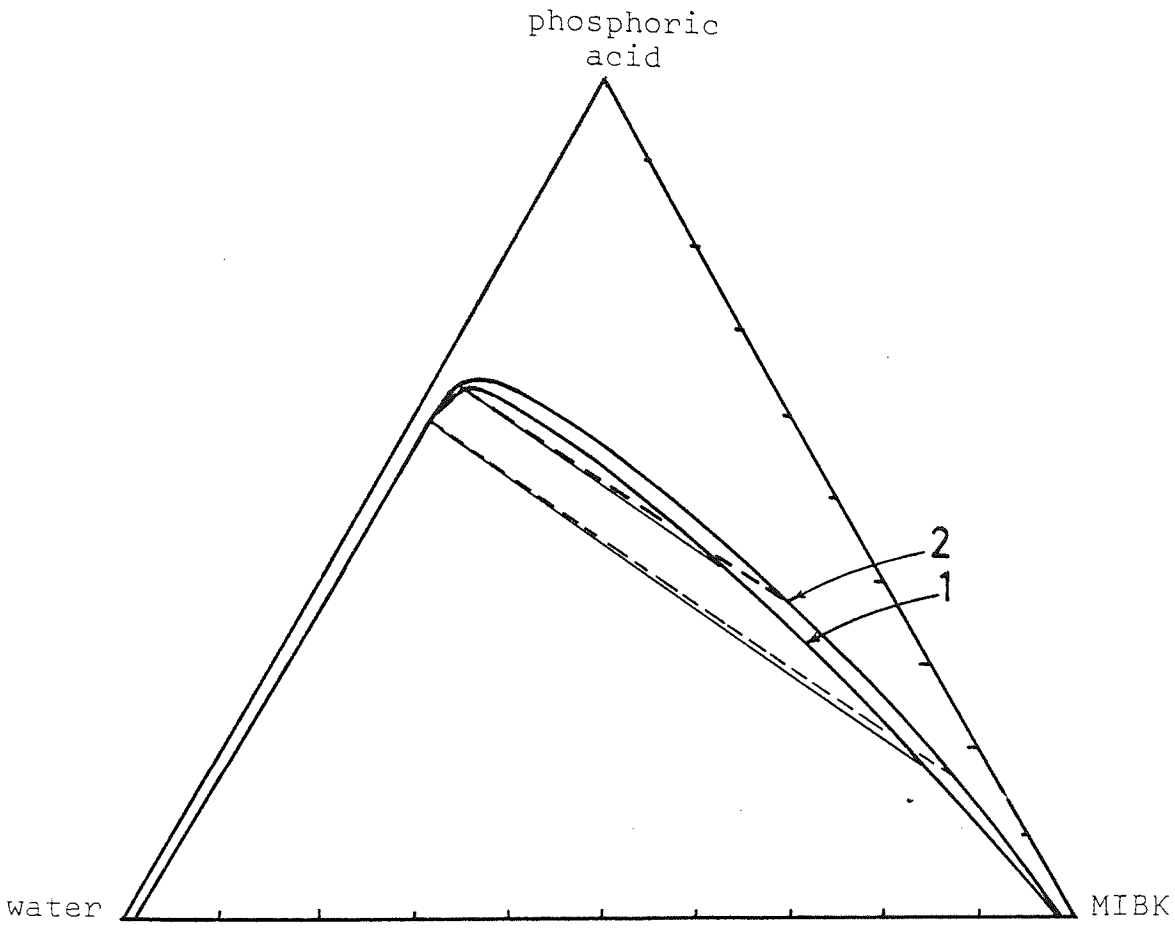


Fig.7.15 Comparison between the phase equilibrium diagrams at 25°C

1. for pure system
2. for impure system

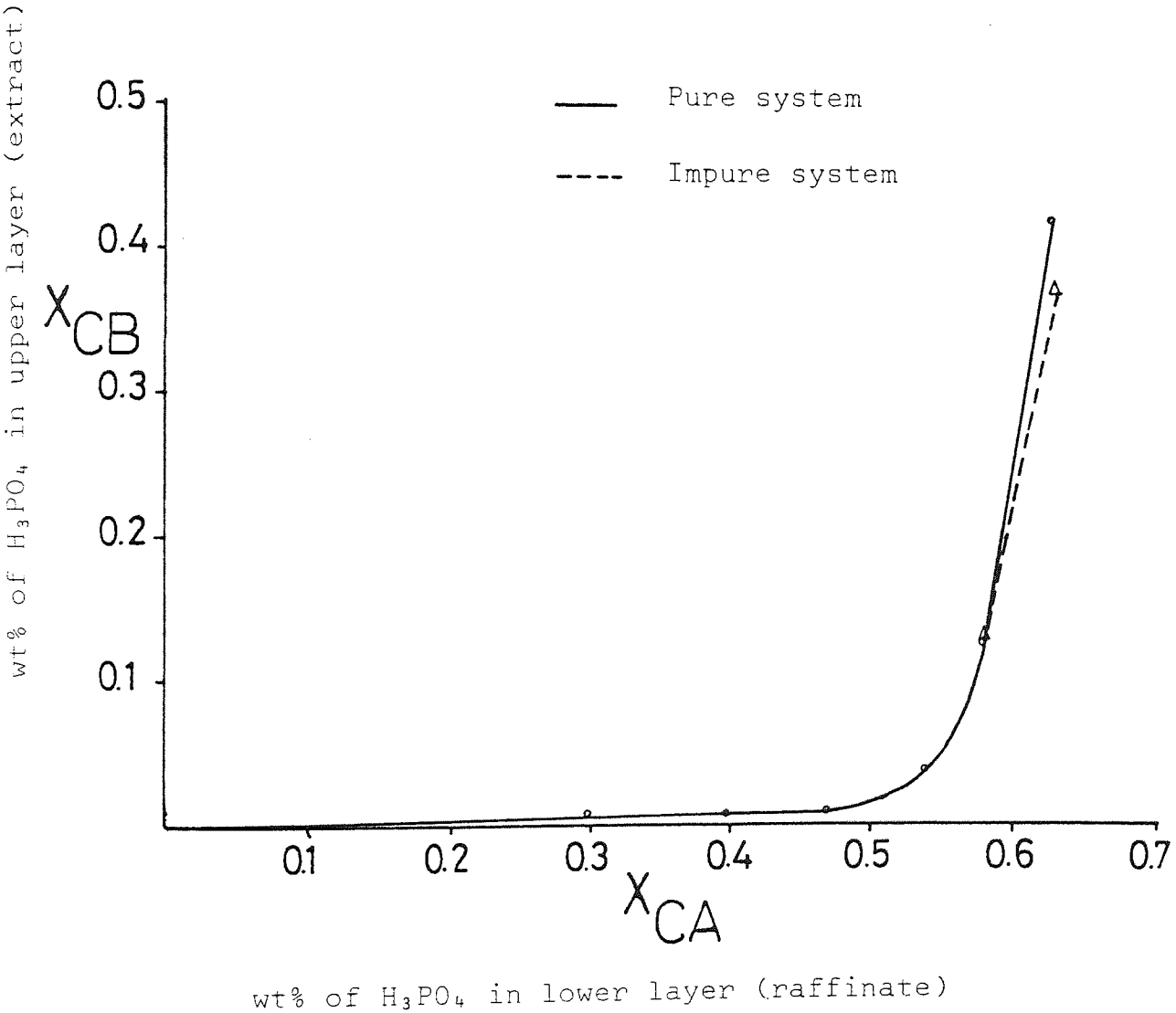


Fig.7.16 Distribution curve for phosphoric acid in the system water - phosphoric acid - methyl-isobutyl ketone at 25°C

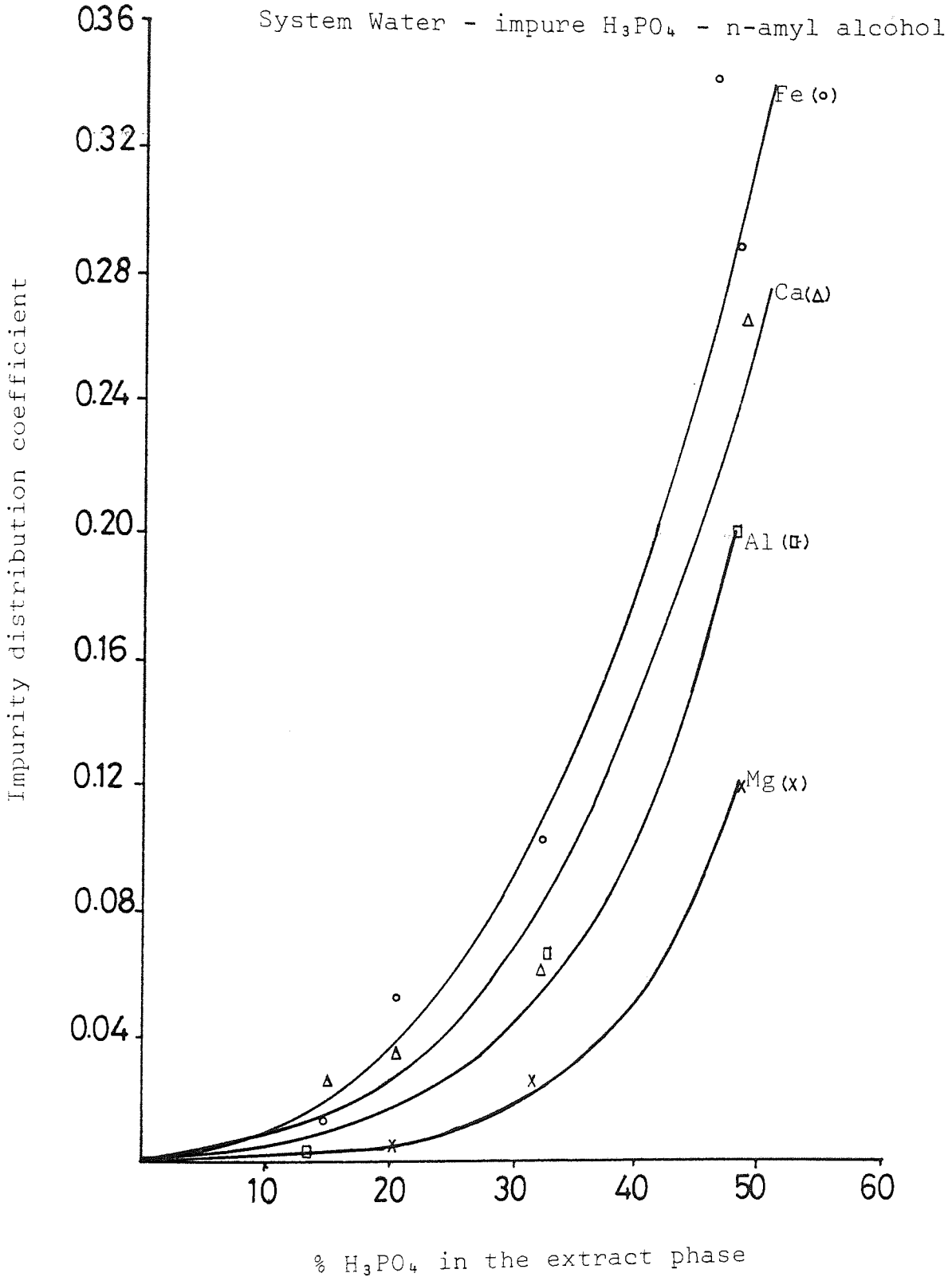


Fig. 7.17 Effect of H_3PO_4 concentration on the impurity distribution coefficient at 0.3 - 0.6% impurity concentration in the feed aqueous acid

System water - impure phosphoric acid - tri-n-butyl phosphate

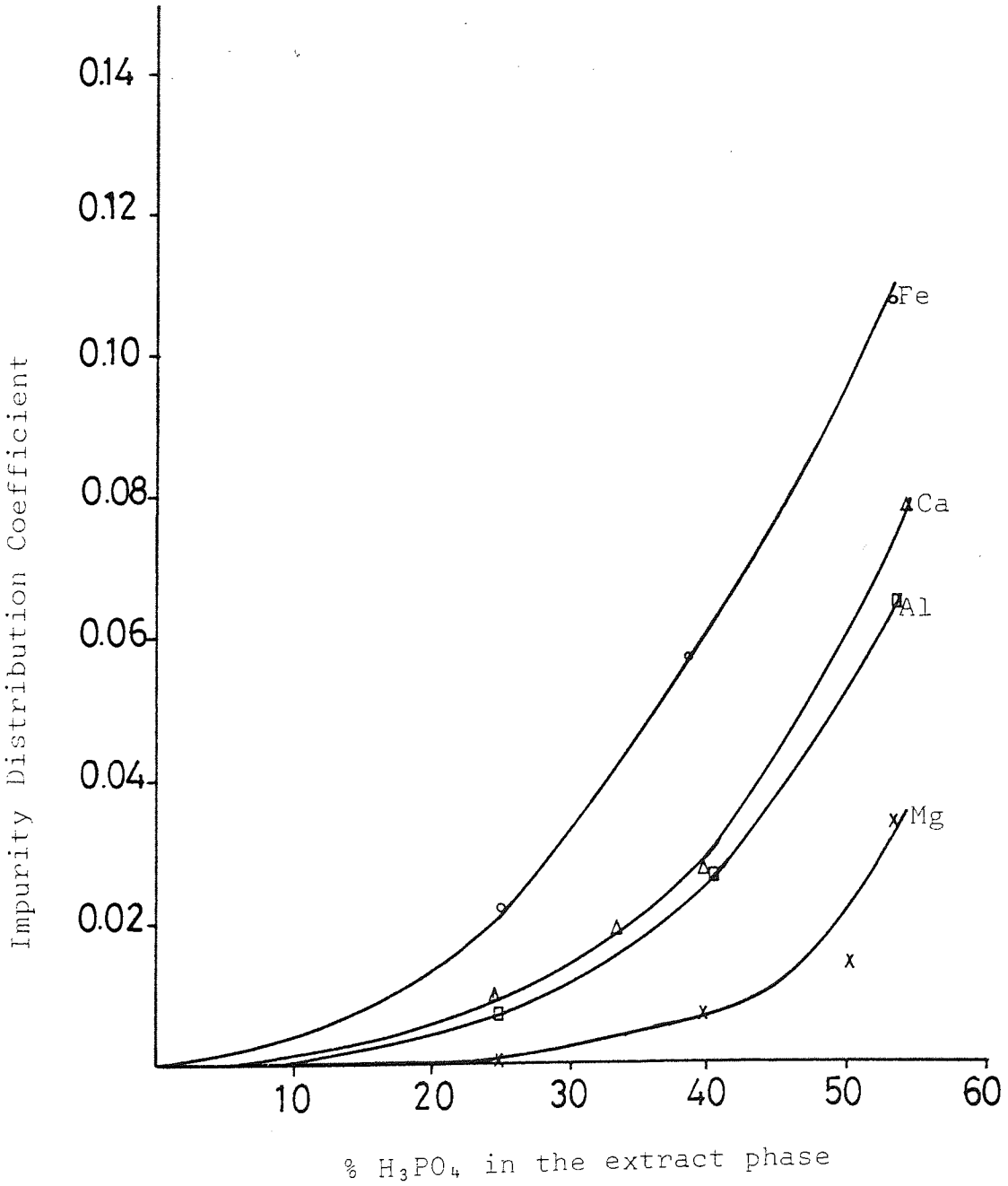


Fig.7.18 Effect of H_3PO_4 concentration on the distribution coefficient of impurities at 0.3 - 0.6% impurity in the feed aqueous impure acid.

System Water - impure H_3PO_4 - di-isopropyl ether

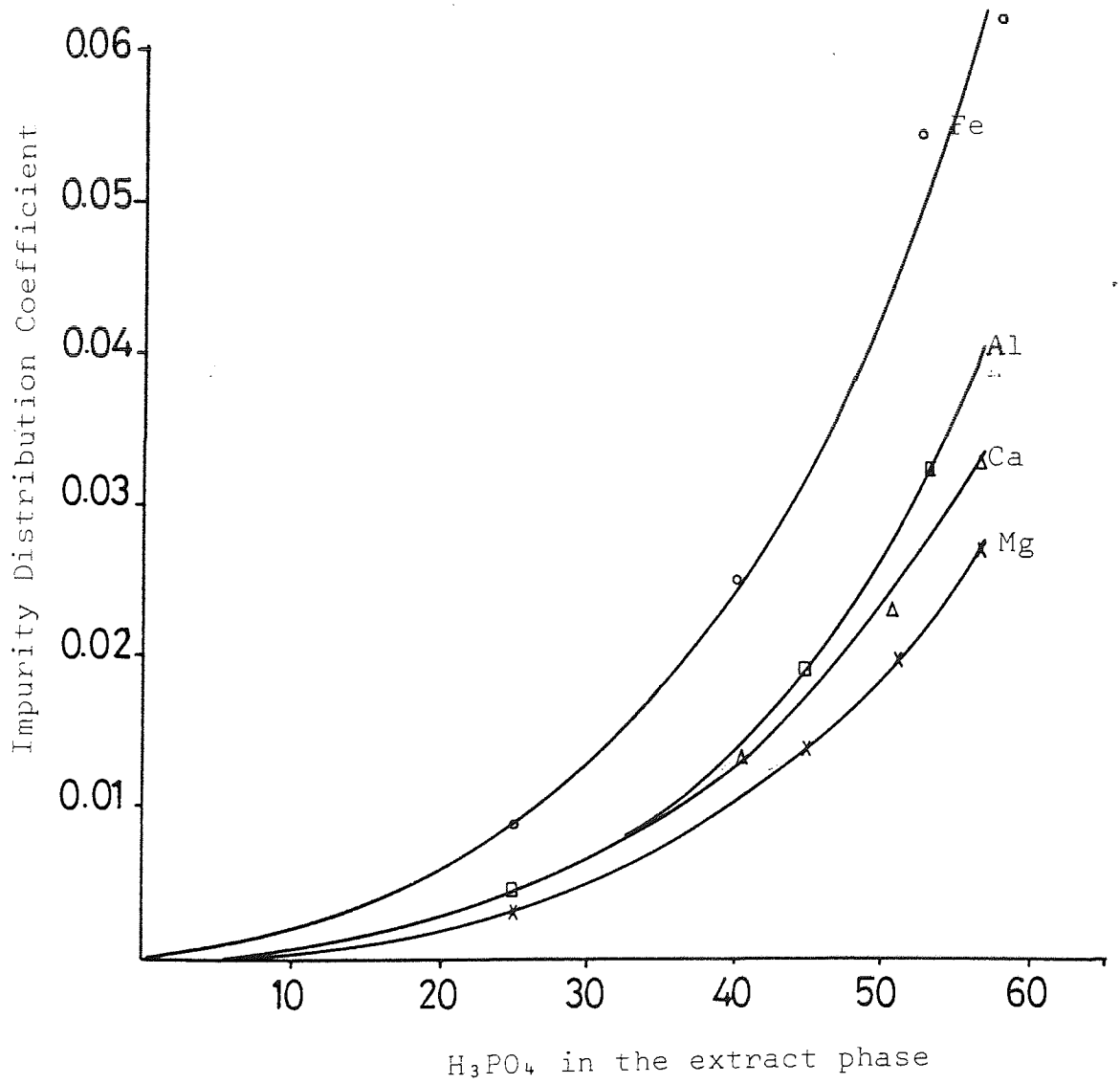


Fig.7.19 Effect of H_3PO_4 concentration in the extract phase on the distribution coefficient at 0.3 - 0.6% impurity concentration in the feed aqueous phase

System water - impure H_3PO_4 - Methyl iso-butyl ketone

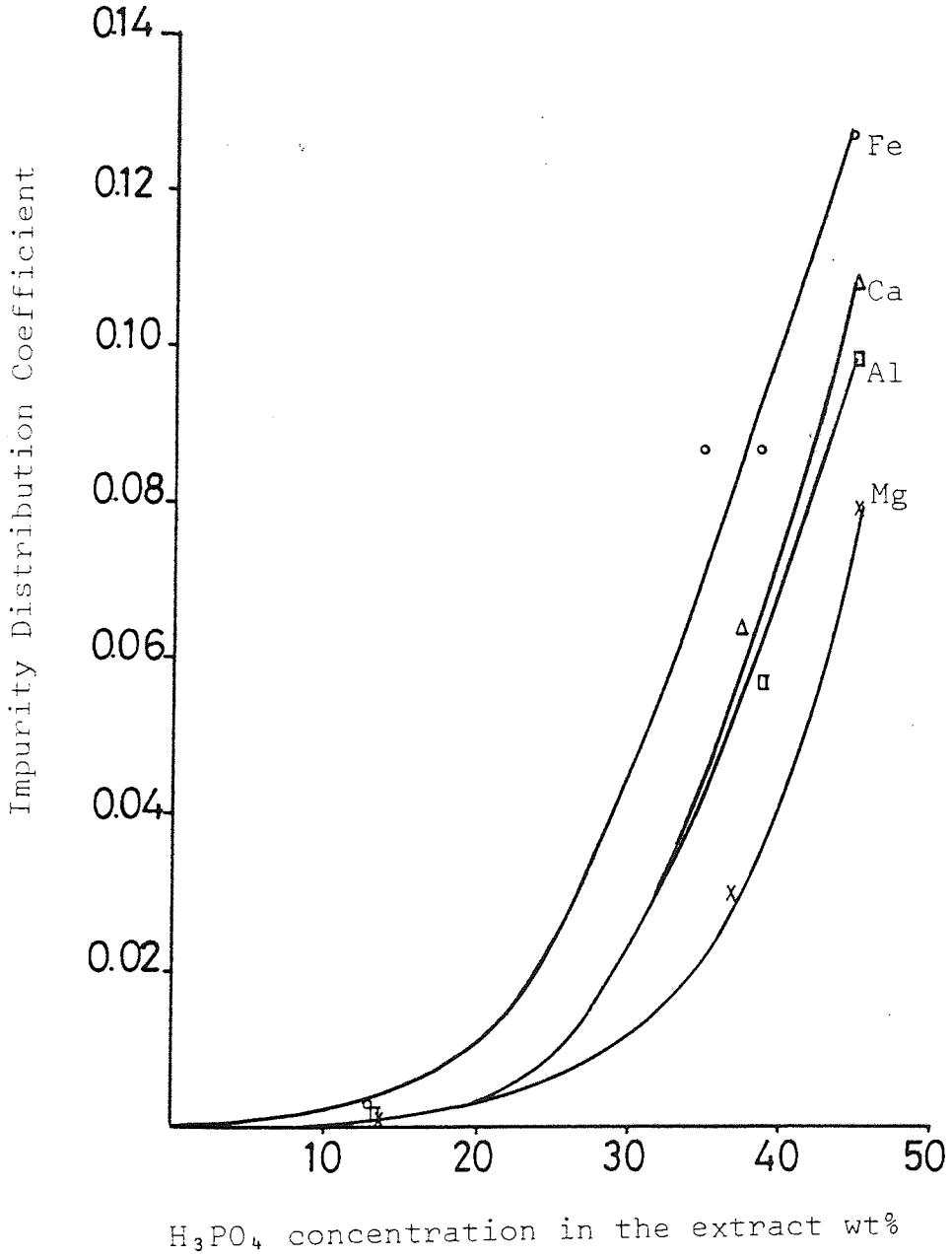


Fig.7.20 Effect of H_3PO_4 concentration in the extract phase on the impurity distribution coefficient at 0.3 - 0.6% impurity concentration in the feed aqueous acid

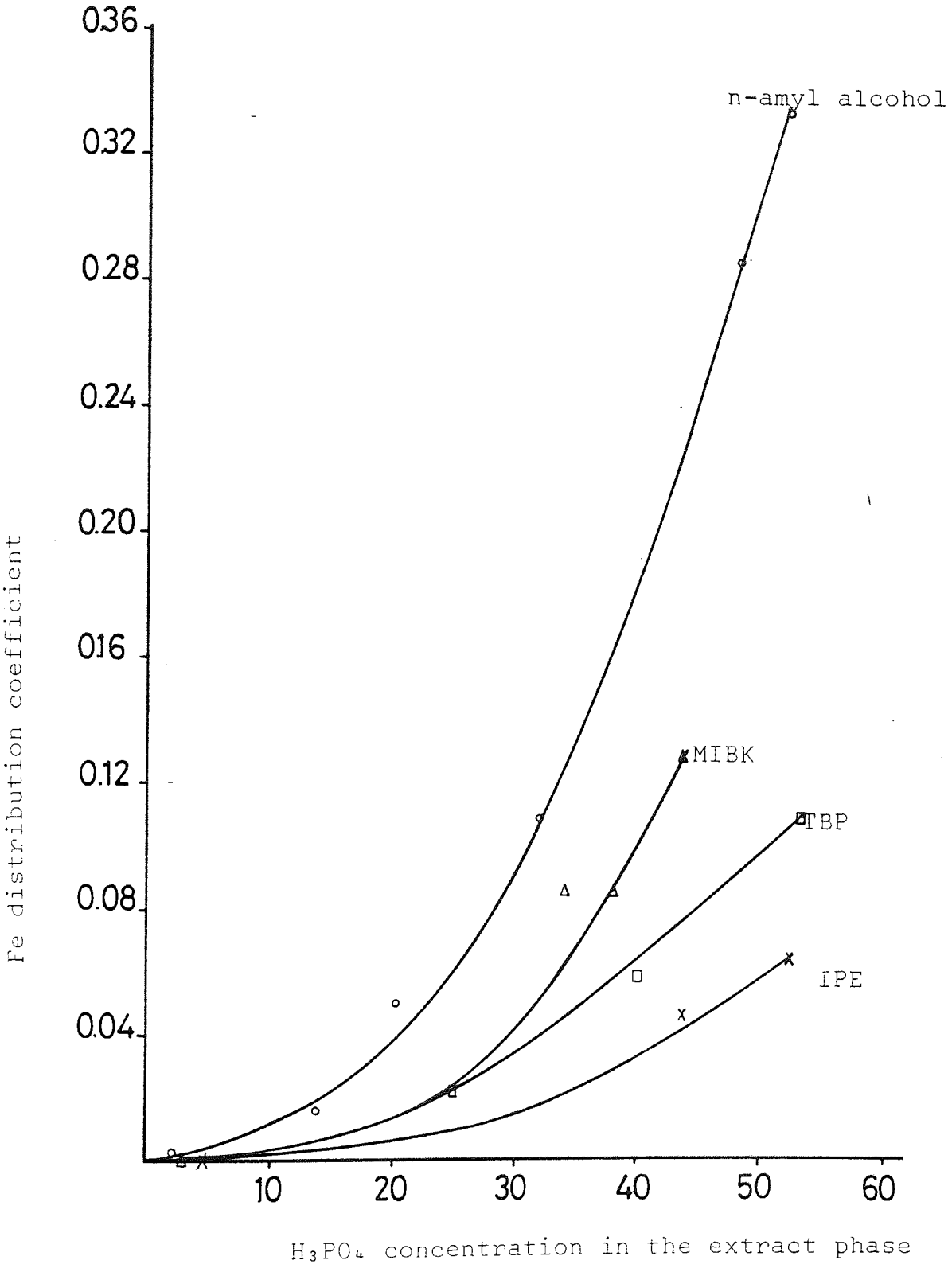
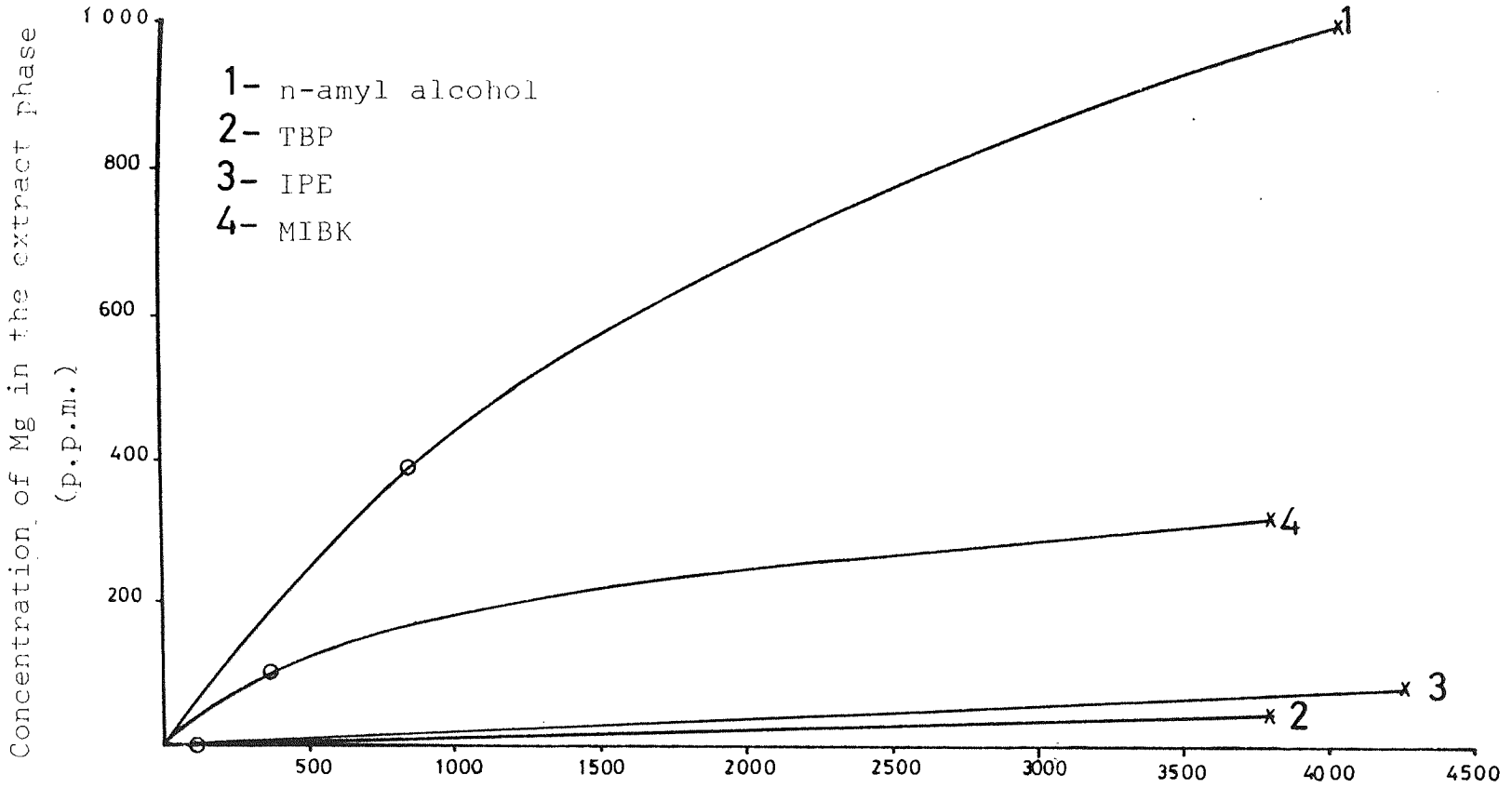


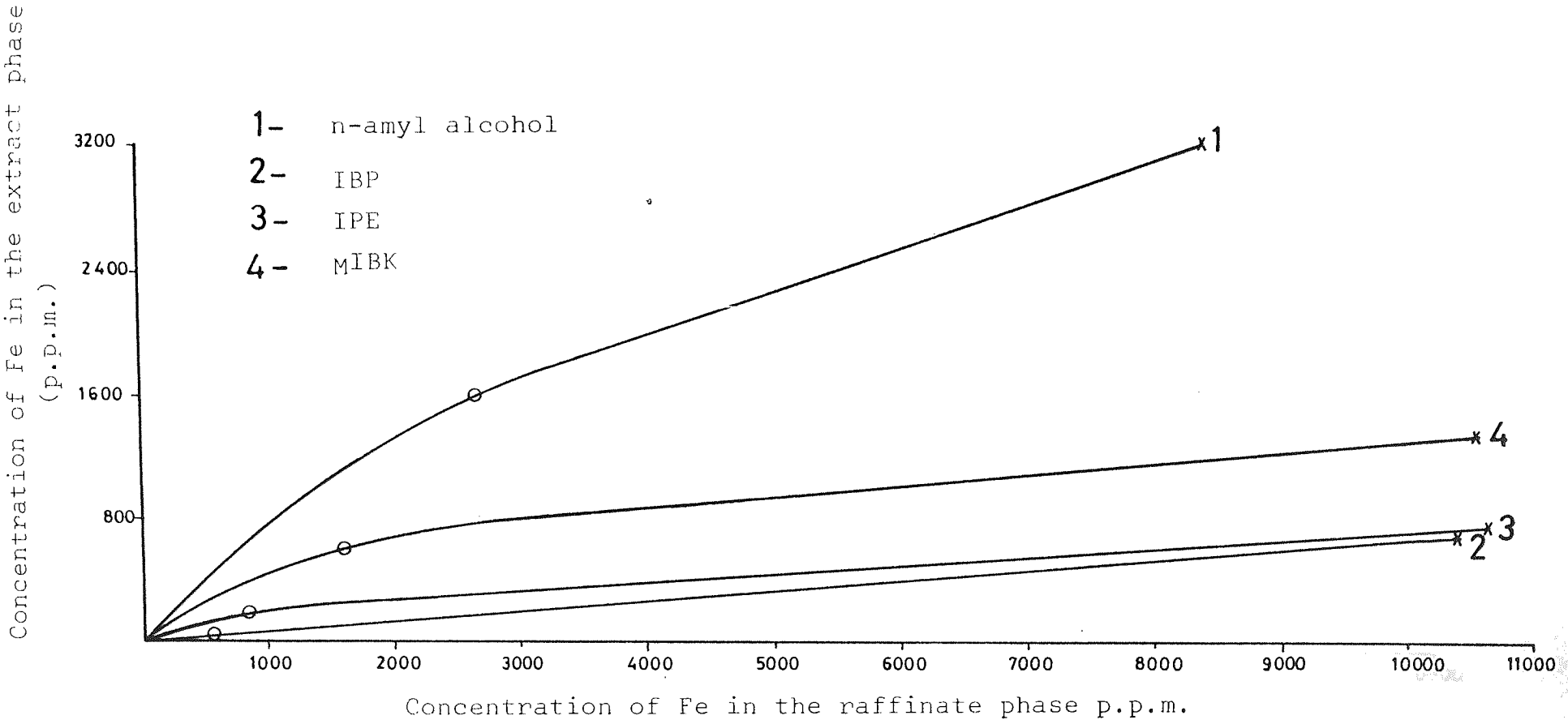
Fig.7.21 Comparison of the effect of H_3PO_4 concentration in the extract phase on the distribution coefficient of the Fe^{3+} at 0.5% Fe concentration in the aqueous feed



x - Represents an extraction stage of wet-process acid with pure solvent

o - Represents a purification stage of the extract (from extraction step) with pure acid

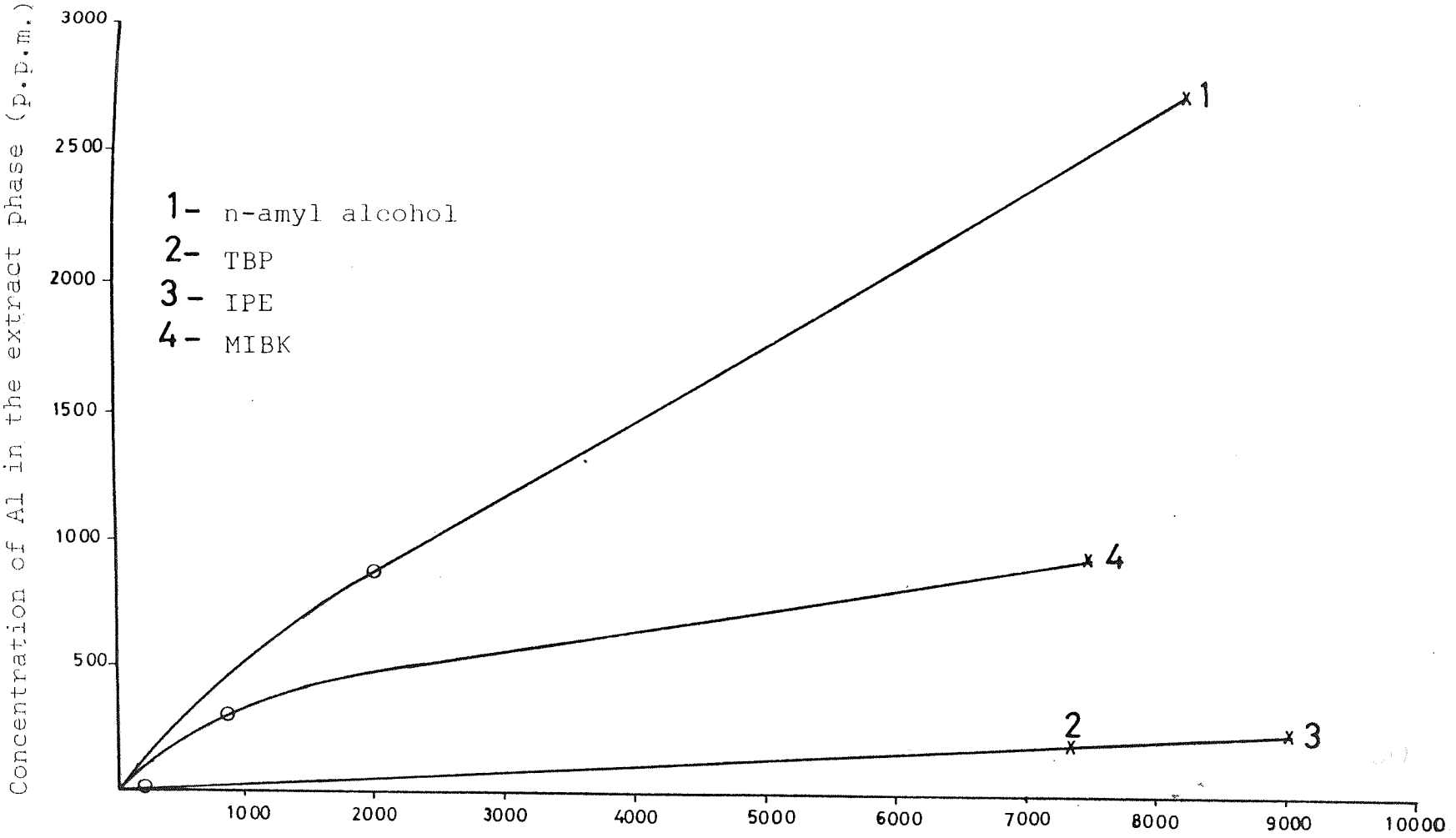
Fig.7.22 Distribution curve for Mg in the system water - 54% P_2O_5 wet - process phosphoric acid - solvent at 25°C



x - Represents an extraction stage of wet-process acid with pure solvent

o - Represents a purification stage of extract (from extraction step) with pure acid

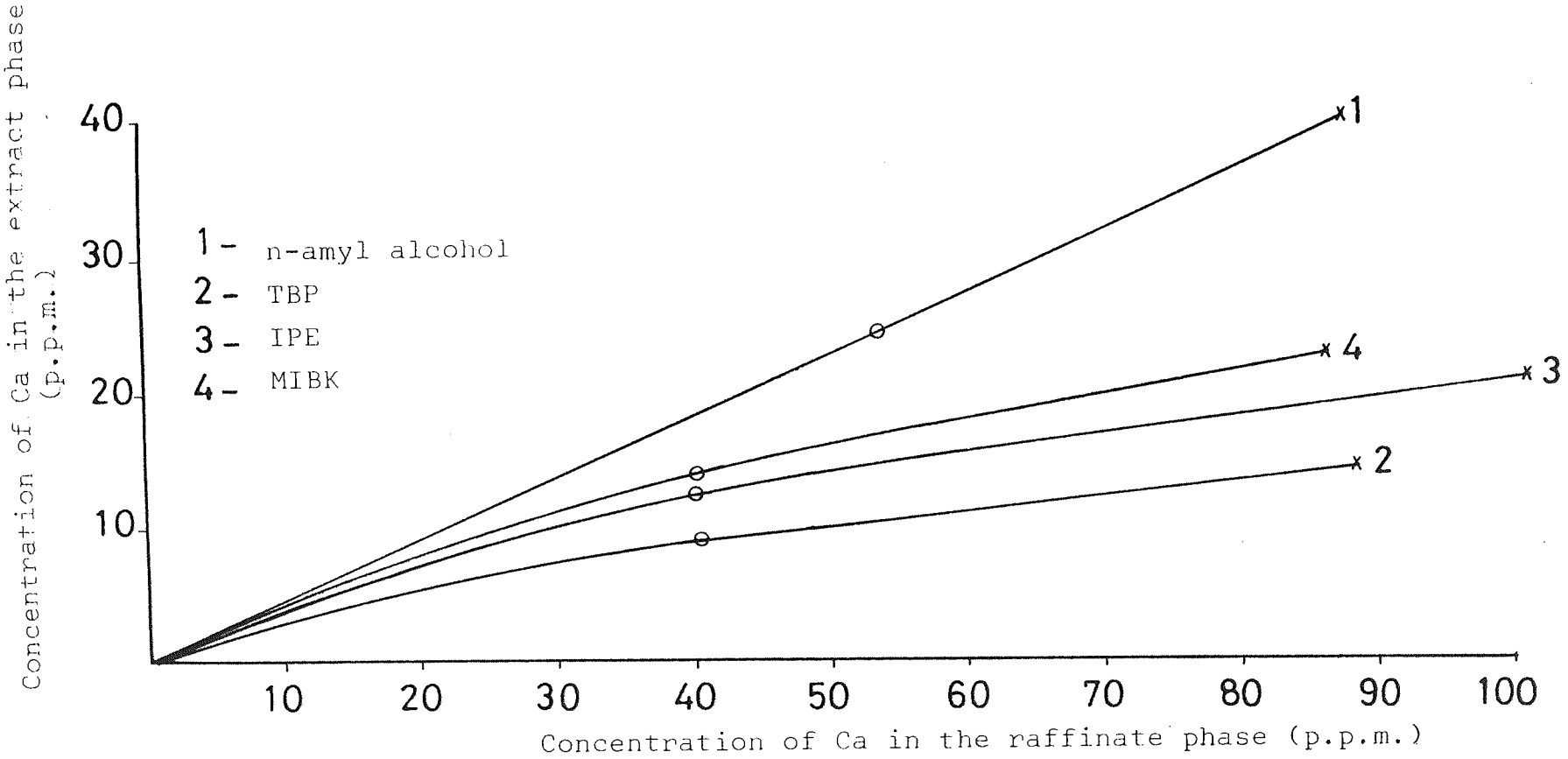
Fig.7.23 Distribution curve for Fe in the system water - 54% P_2O_5 wet-process phosphoric acid - solvent at 25^oC



x - Represents an extraction stage of wet-process acid with pure solvent

o - Represents a purification stage of extract from extraction step with pure acid

Fig.7.24 Distribution curve for Al in the system water - 54% P_2O_5 wet process phosphoric acid - solvent at $25^{\circ}C$



x - Represents an extraction stage of wet-process acid with pure solvent

o - Represents a purification stage of the extract (from extraction step) with pure acid

Fig.7.25 Distribution curve for Ca in the system water - 54% P_2O_5 wet process phosphoric acid - solvent at 25^oC

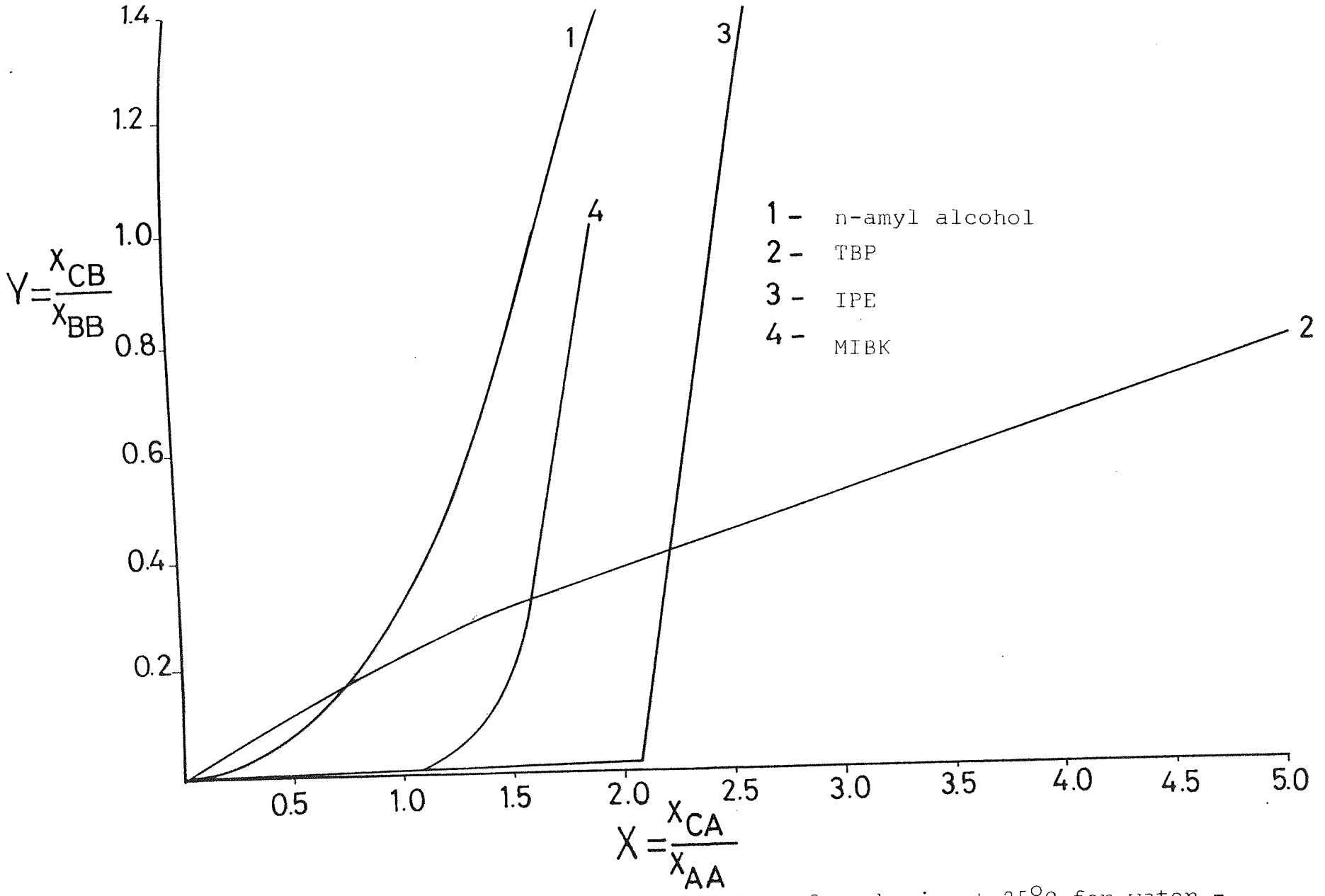


Fig.7.26 Distribution curve of H_3PO_4 on solute free-basis at 25°C for water - phosphoric acid - solvent

7.2 RESULTS FROM HYDRODYNAMIC STUDIES

As mentioned earlier, the phase ratio of water to solvent was kept constant at 1:1 by weight for all the solvent systems with water and phosphoric acid. At this ratio and at a 200gms total batch size the impeller was always immersed in the aqueous phase. The position of the interface was generally lowered by an increase of acid concentration due to the increase in the aqueous phase density. This meant that the impeller became closer to the interface. No attempts were made to alter the position of the impeller.

7.2.1 Effect of Energy Input and H_3PO_4 Concentration

In all cases, the drop-size of the dispersed phase decreased with an increase of phosphoric acid concentration and agitator speed as shown in Figures 7.27 to 7.37. However, the rate of drop size reduction generally decreased with increasing agitator speed and H_3PO_4 concentration, provided the same dispersion pattern prevailed. The lowest agitator speed to cause complete dispersion of one phase into the other also decreased with increase of H_3PO_4 concentration in each system.

For the purpose of describing the phase dispersion only, the acid concentration in the system can be divided into three regions, low, medium and high and these regions vary with the solvent under consideration. It was noted that with all systems, except tri-n-butyl phosphate, the stable dispersion

at low acid concentrations was aqueous phase in solvent phase (W/O), but as the concentration was increased reaching the medium region, the system could be inverted to O/W if the agitator was started at low speed (low energy input). At high acid concentrations the system could not be made W/O even when starting the agitator at high speed. The opposite is also true for a system within the low acid concentration region. Therefore, it was only possible to achieve dispersions of either phase in the medium concentration region. Phase dispersion was detected from the manner in which coalescence took place after switching off the stirrer, as shown in Figure 7.46.

The phase inversion was always accompanied by a change in the drop size and settling time. When the systems were inverted from W/O to O/W the drop size decreased and the settling time increased. However, as the acid concentration moved out of the medium region, secondary dispersions were formed when the system was W/O and the time required for settling was longer than 24 hours in some cases. Fortunately at high acid concentrations where the system was always O/W, the settling time was not appreciably affected by an increase of acid concentration, until this became very high. Even then settling took less than 30 minutes. The effect of phase inversion on drop size can be seen in Figures 7.32 and 7.33 for di-iso propyl ether and Figures 7.35 and 7.37 for methyl isobutyl ketone; and on the settling time in Figures 7.38 and 7.39.

With tri-n-butyl phosphate systems the pattern of phase inversion was different. It was possible within the whole

concentration region studied to disperse either phase. The settling time was generally longer when the system was W/O although no secondary dispersions were obtained when operating with W/O systems as shown in Figures 7.38 and 7.39. The drop size for 15% H_3PO_4 concentration (Figure 7.29) was smaller when the system was W/O which is different from other systems.

7.2.2 Effect of Impurities

The effect of impurities on drop size was studied for di-isopropyl ether and methyl isobutyl ketone systems (Figures 7.31 to 7.37). However, no clear trend was obtained. In some cases the drop size decreased while in other similar cases the drop size increased or remained similar to the pure system.

The effect of impurities on the settling time, however, was clearer and is summarised in Figures 7.40 to 7.42. In general the presence of impurities lengthened the settling time for mixtures containing relatively low acid concentrations while it shortened it for mixtures containing high acid concentrations. The extent and order of influence of the impurities was not consistent for the different solvent systems.

7.2.3 Effect of Agitator Speed on Settling Time

The effect of agitator speed on settling time is summarised in Figures 7.43 to 7.45. It can be concluded that within the agitator speeds studied, the settling time was generally

constant at different speeds except in a few cases where it was shorter at very low speeds. Complete dispersion of one phase into the other was established for all systems at the lowest speed before any measurements were taken.

1- 15% H_3PO_4 of total batch

2- 30% H_3PO_4 of total batch

3- 45% H_3PO_4 of total batch

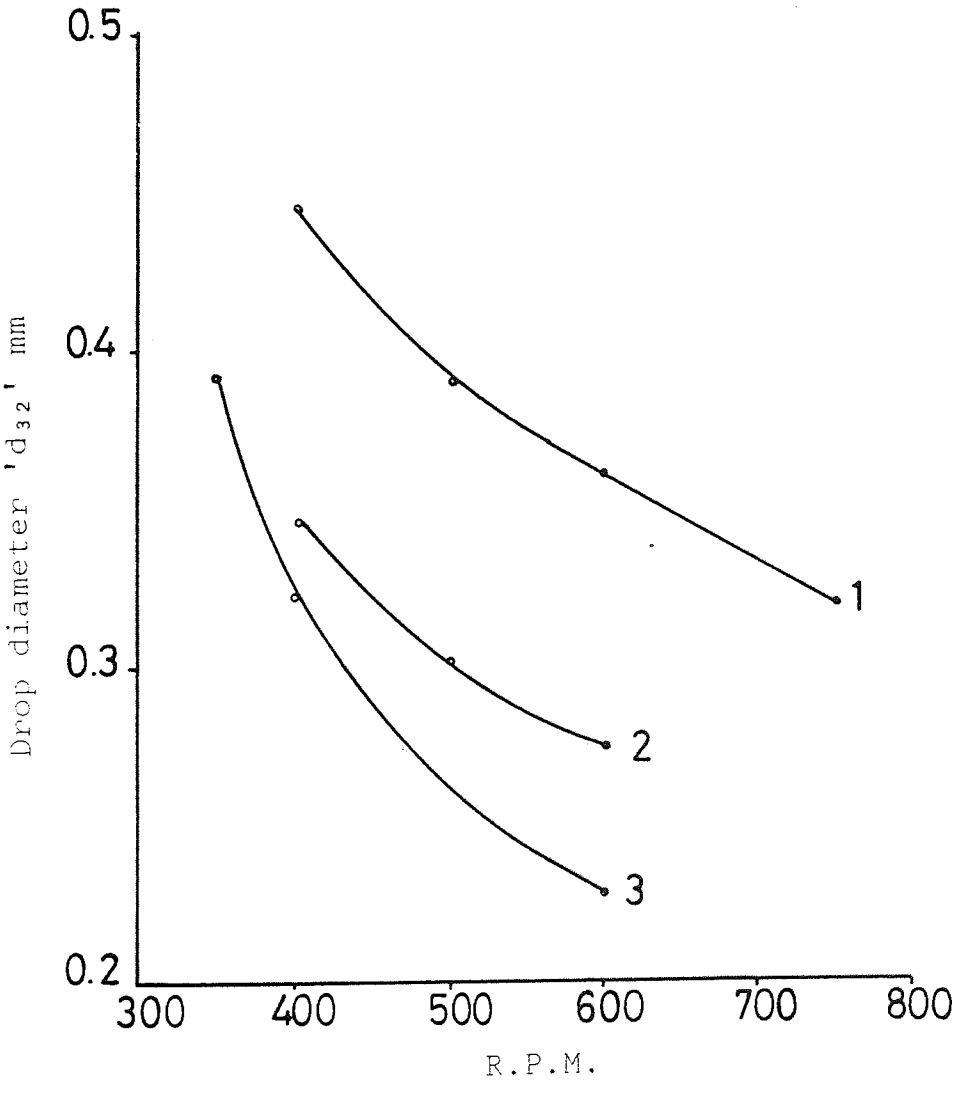


Fig.7.27 Drop size vs. Agitator speed (RPM), system water - phosphoric acid - n-amyl alcohol at 25°C, mixtures at 1:1 by weight water to solvent. (O/W)

1- at 500 RPM

2- at 600 RPM

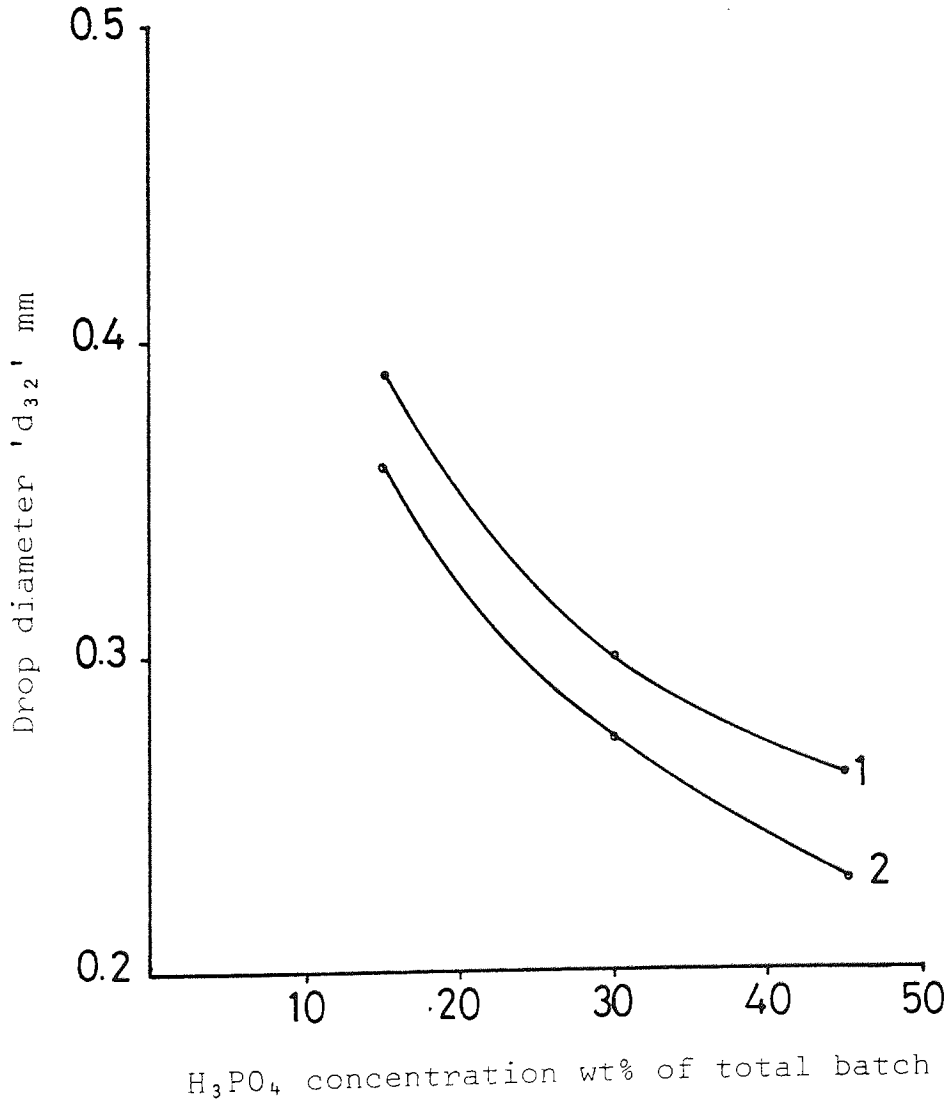


Fig.7.28 Drop-size vs. H_3PO_4 concentration, system: water - phosphoric acid - n-amyl alcohol at 25°C., mixtures at 1:1 by weight water to solvent. (O/W)

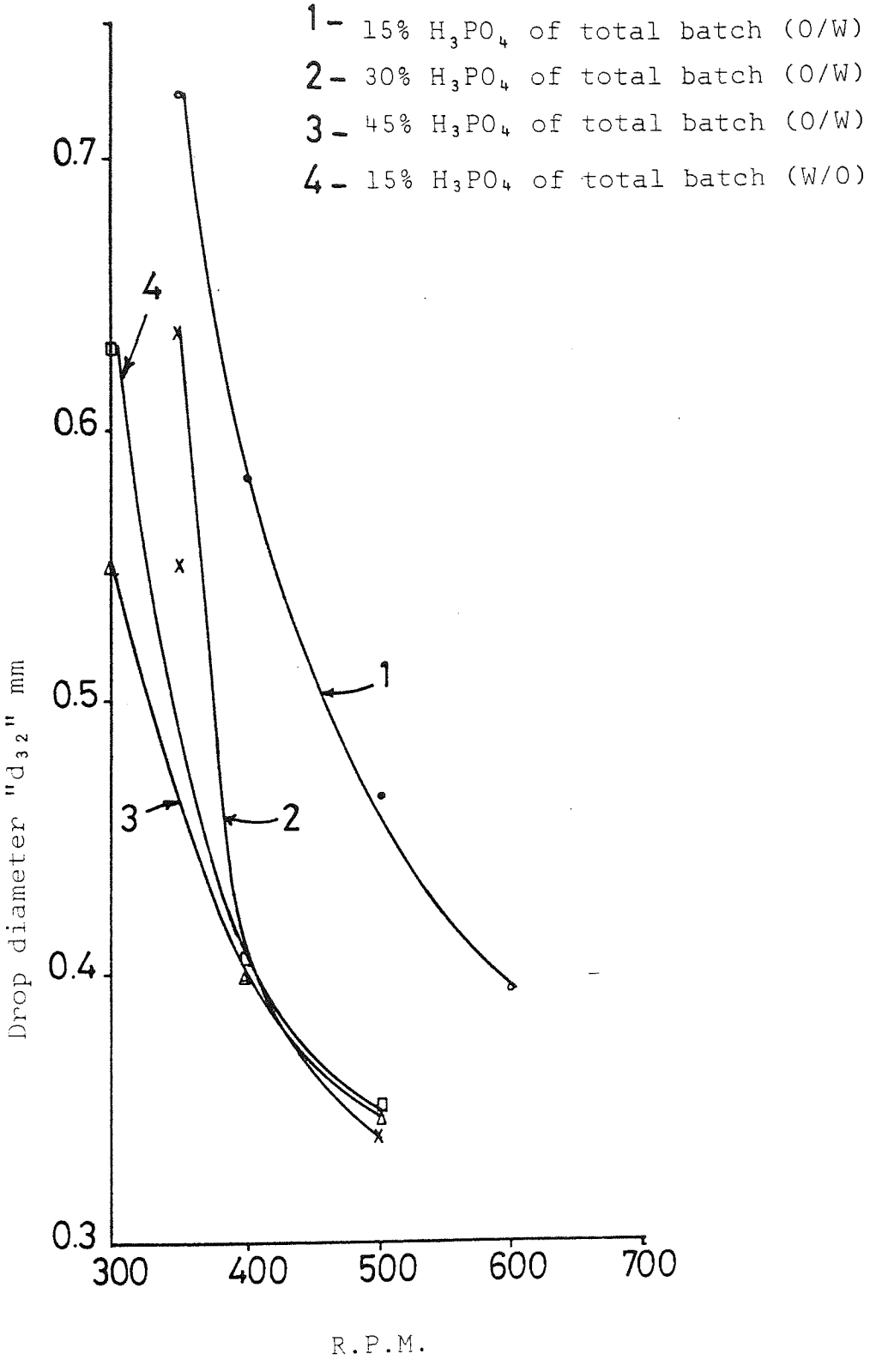


Fig.7.29 Drop size vs. agitator speed (RPM), system: water - phosphoric acid - tri-n-butyl phosphate. Mixtures at 1:1 by weight water to solvent

1- 400 R.P.M.

2- 500 R.P.M.

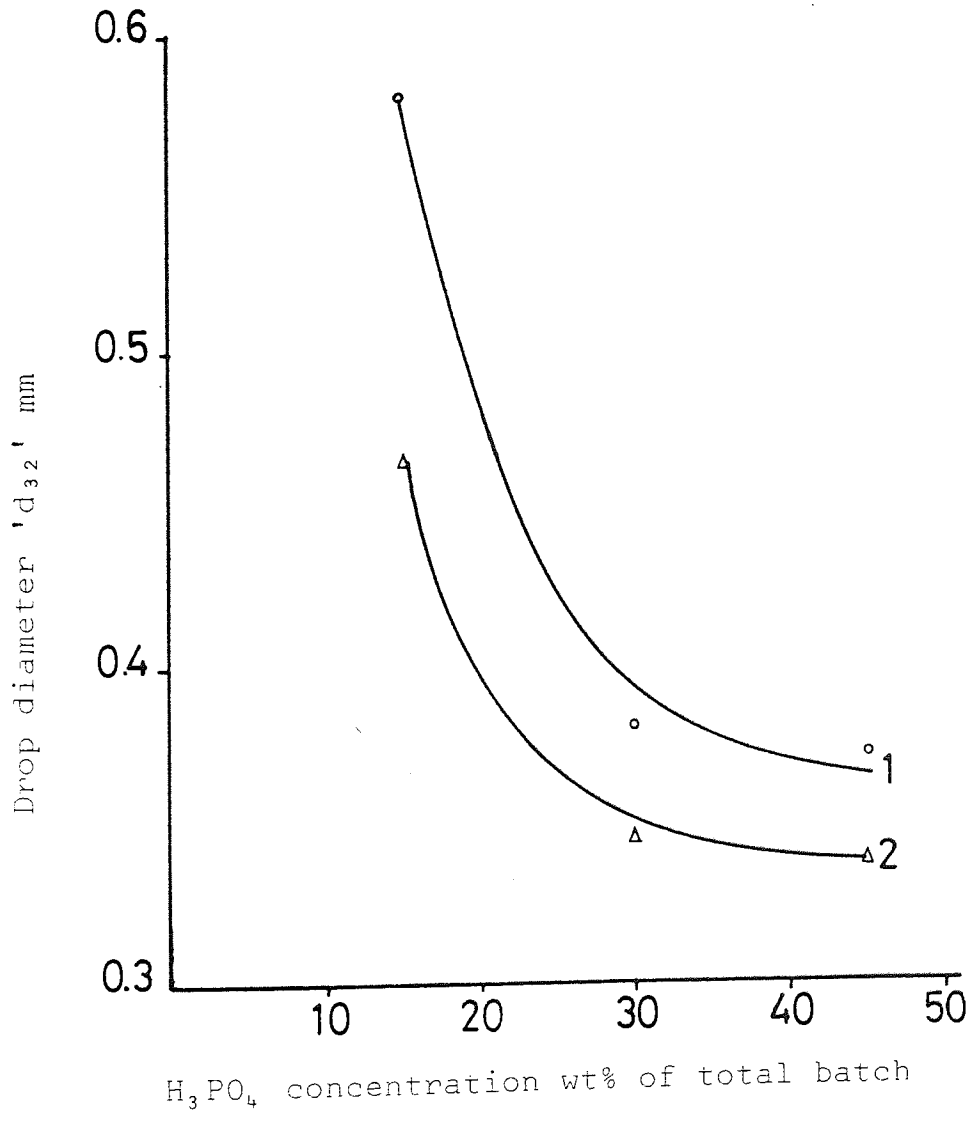


Fig.7.30 Drop size vs. H_3PO_4 concentration system water - phosphoric acid - tri-n-butyl phosphate mixtures at 1:1 by weight water to solvent. (O/W)

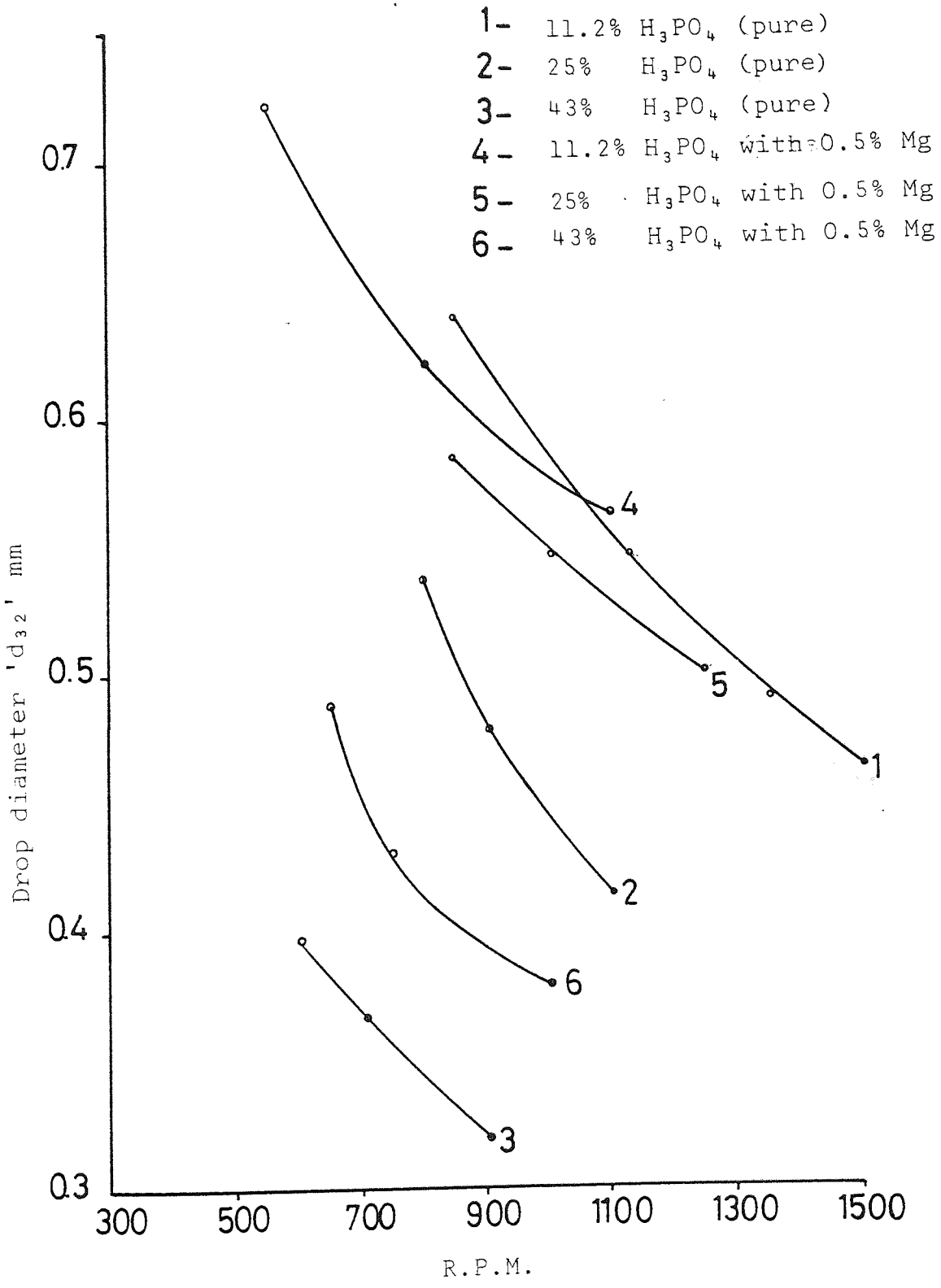


Fig.7.31 Drop size vs. Agitator speed (RPM), system - water - phosphoric acid - di-isopropyl ether at 25°C. Mistures at 1:1 by weight water to solvent. (W/O)

1- 11.2% H_3PO_4 with 0.5% Fe (W/O)
2- 25% H_3PO_4 with 0.5% Fe (W/O)
3- 43% H_3PO_4 with 0.5% Fe (W/O)
4- 43% H_3PO_4 with 0.5% Fe (O/W)

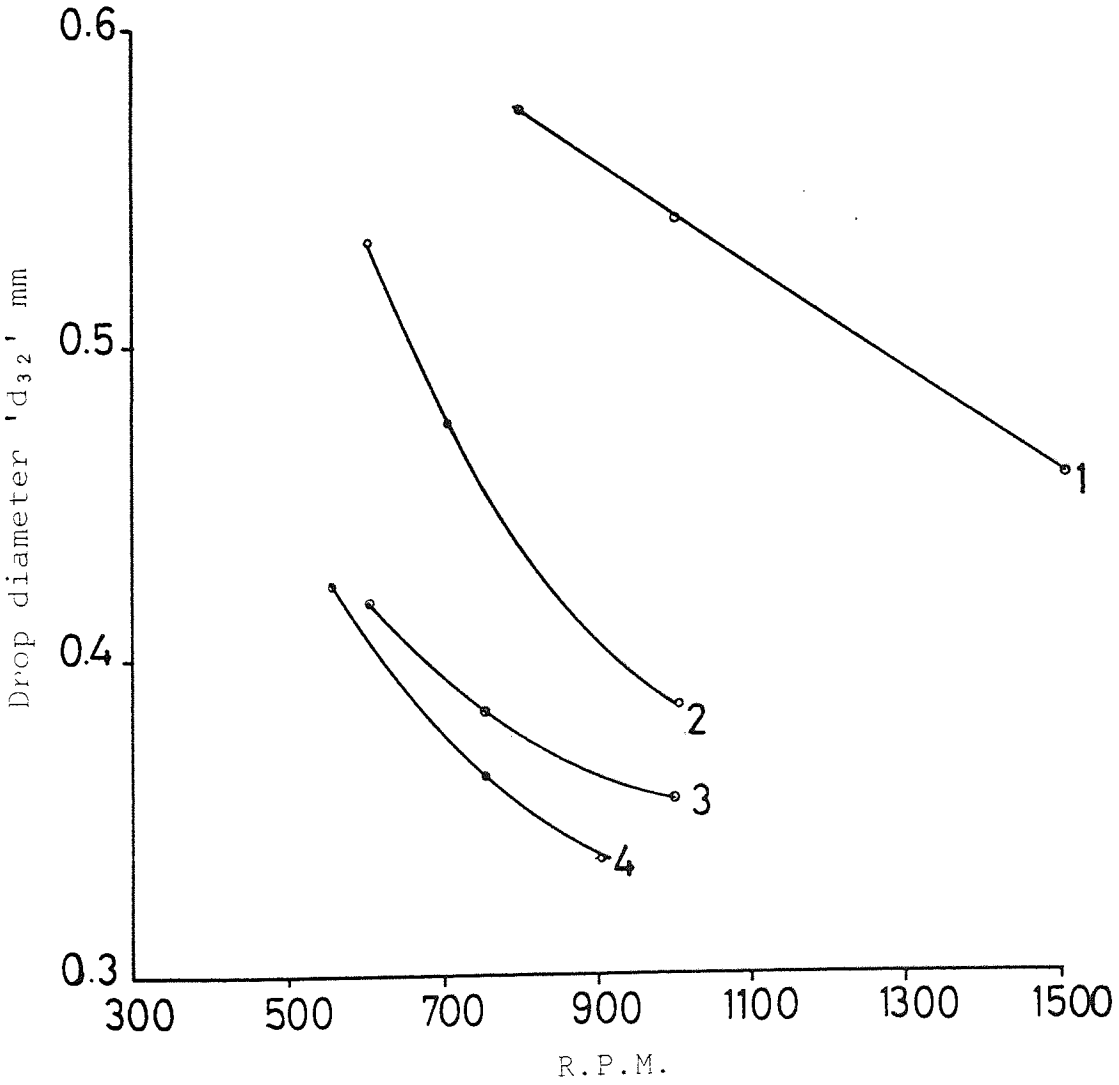


Fig.7.32 Drop size vs. agitator speed (RPM), system: water - phosphoric acid - di-isopropyl ether at 25°C., mixtures at 1:1 by weight water to solvent

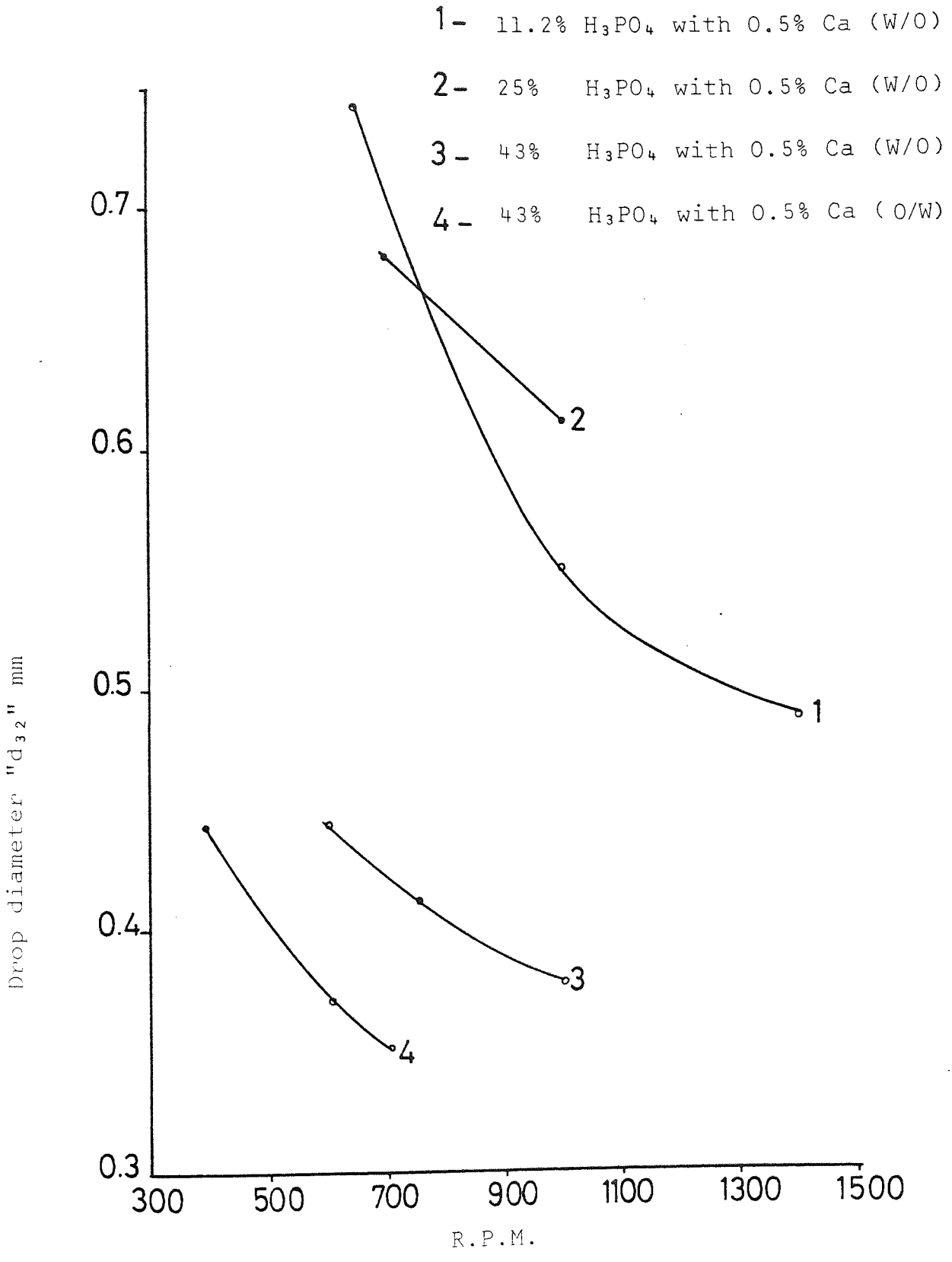


Fig.7.33 Drop size vs. agitator speed(RPM). System: Water - phosphoric acid - di-isopropyl ether at 25°C. Mixtures at 1:1 by weight water to solvent

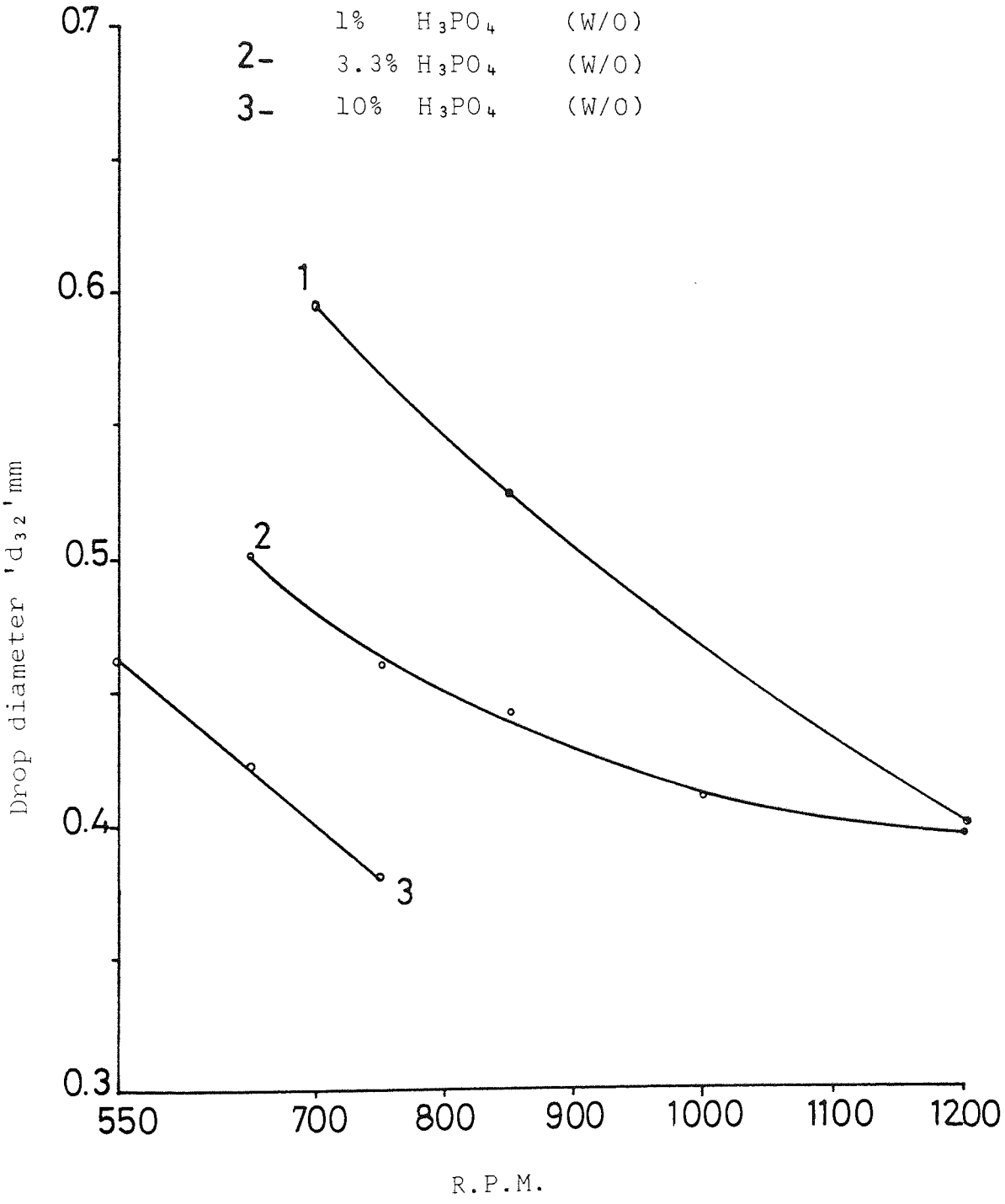


Fig.7.34 Drop size vs. agitator speed (RPM).
System: water - phosphoric acid - methyl iso-butyl ketone at 25°C. Mixtures at 1:1 by weight water to solvent

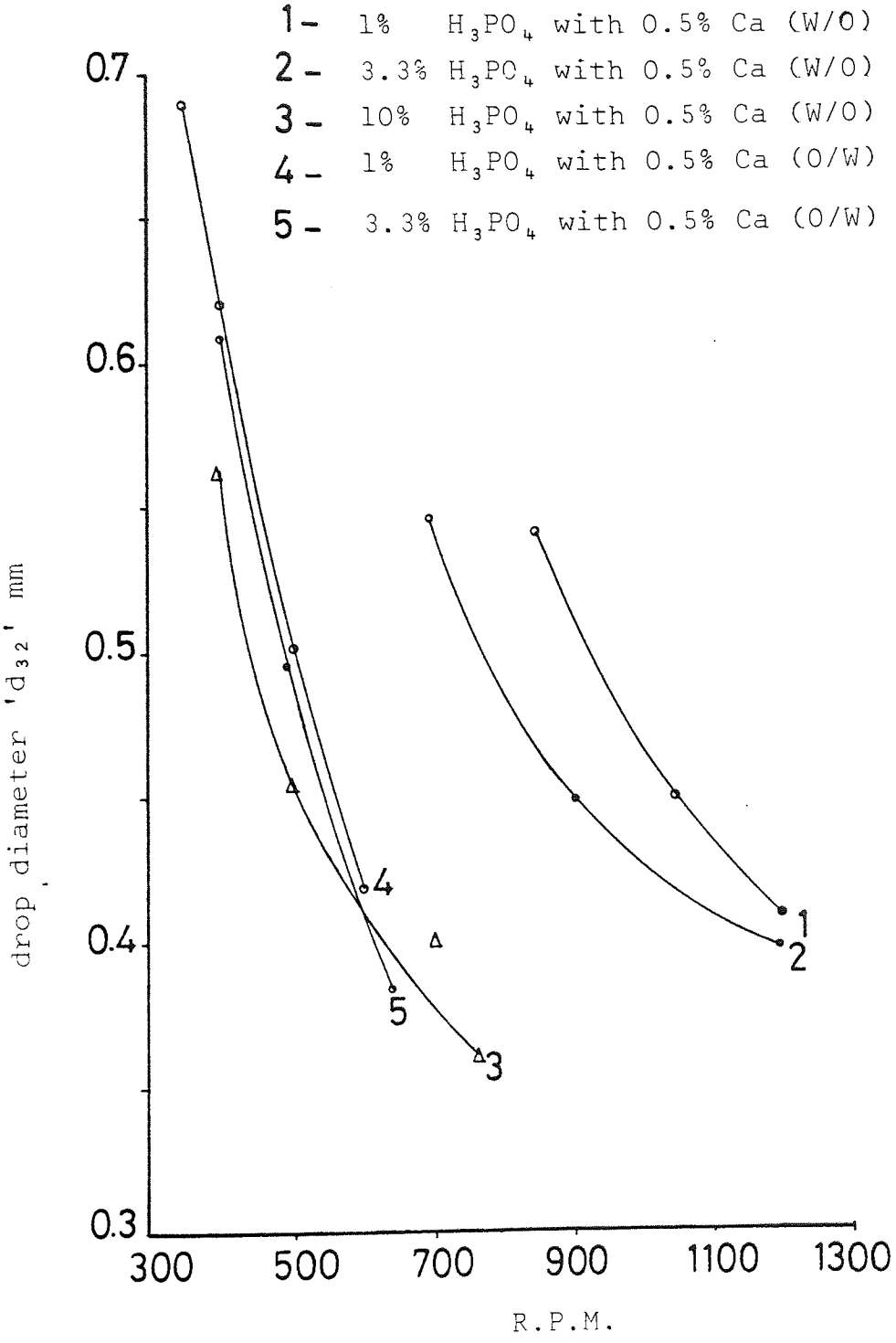


Fig.7.35 Drop size vs. agitator speed (RPM). System: water - phosphoric acid - methyl-isobutyl ketone at 25°C. Mixtures at 1:1 by weight water to solvent.

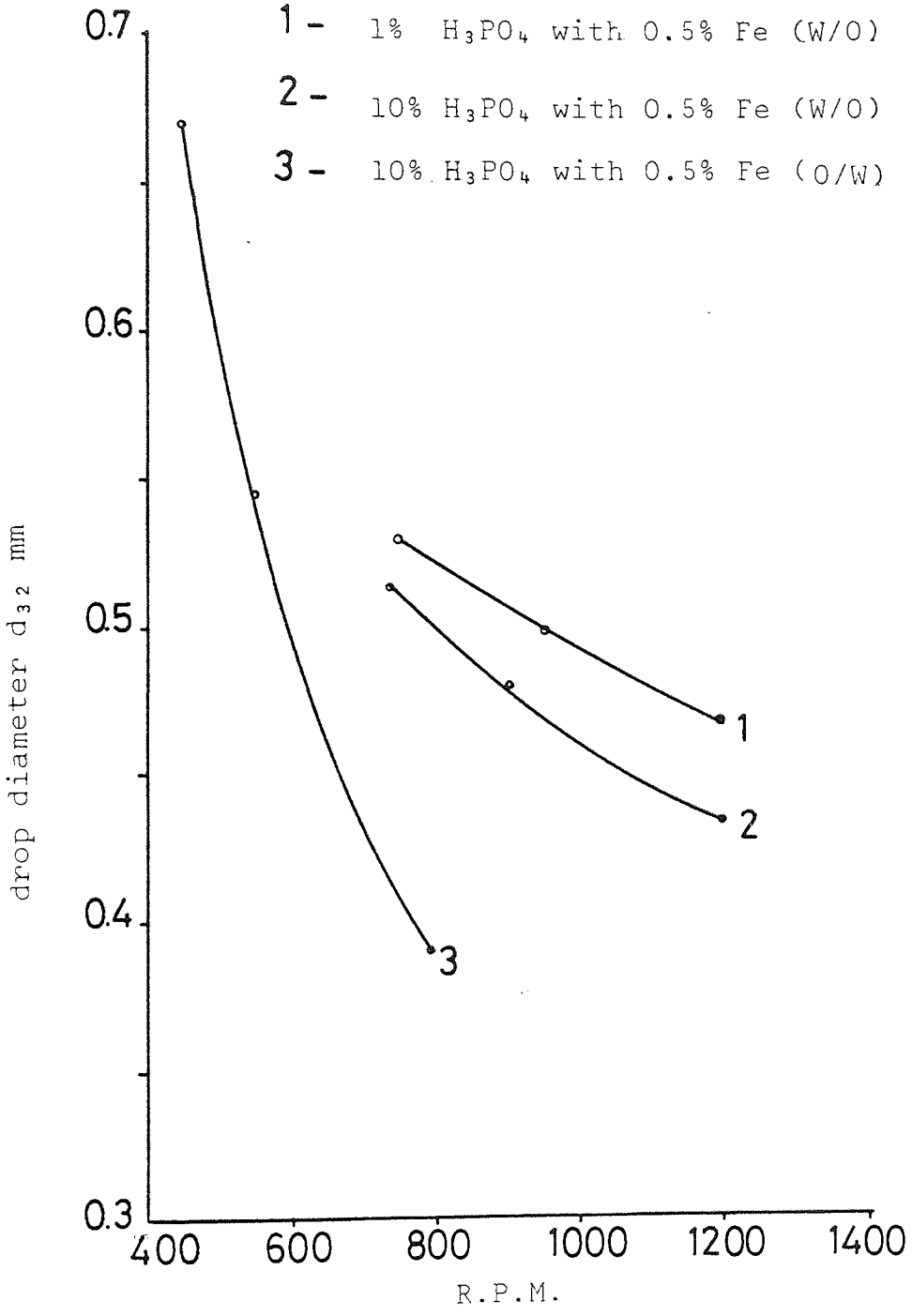


Fig.7.36 Drop size vs. agitator speed (RPM). System: Water - phosphoric acid - methyl isobutyl ketone at 25°C Mixtures at 1:1 by weight water to solvent

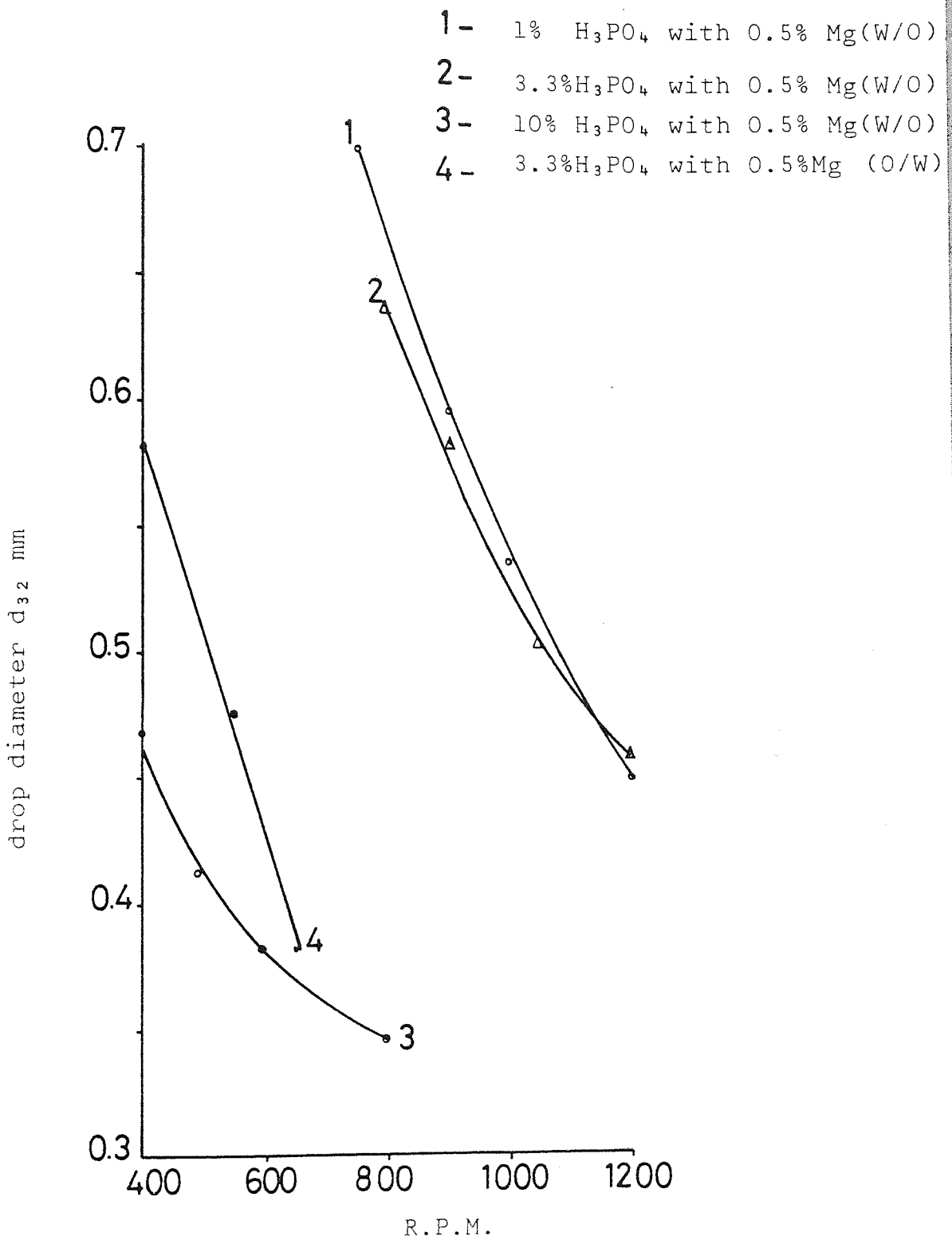


Fig.7.37 Drop size vs. agitator speed (RPM). System: Water - phosphoric acid - methyl iso-butyl ketone at 25°C. Mixtures at 1:1 by weight water to solvent.

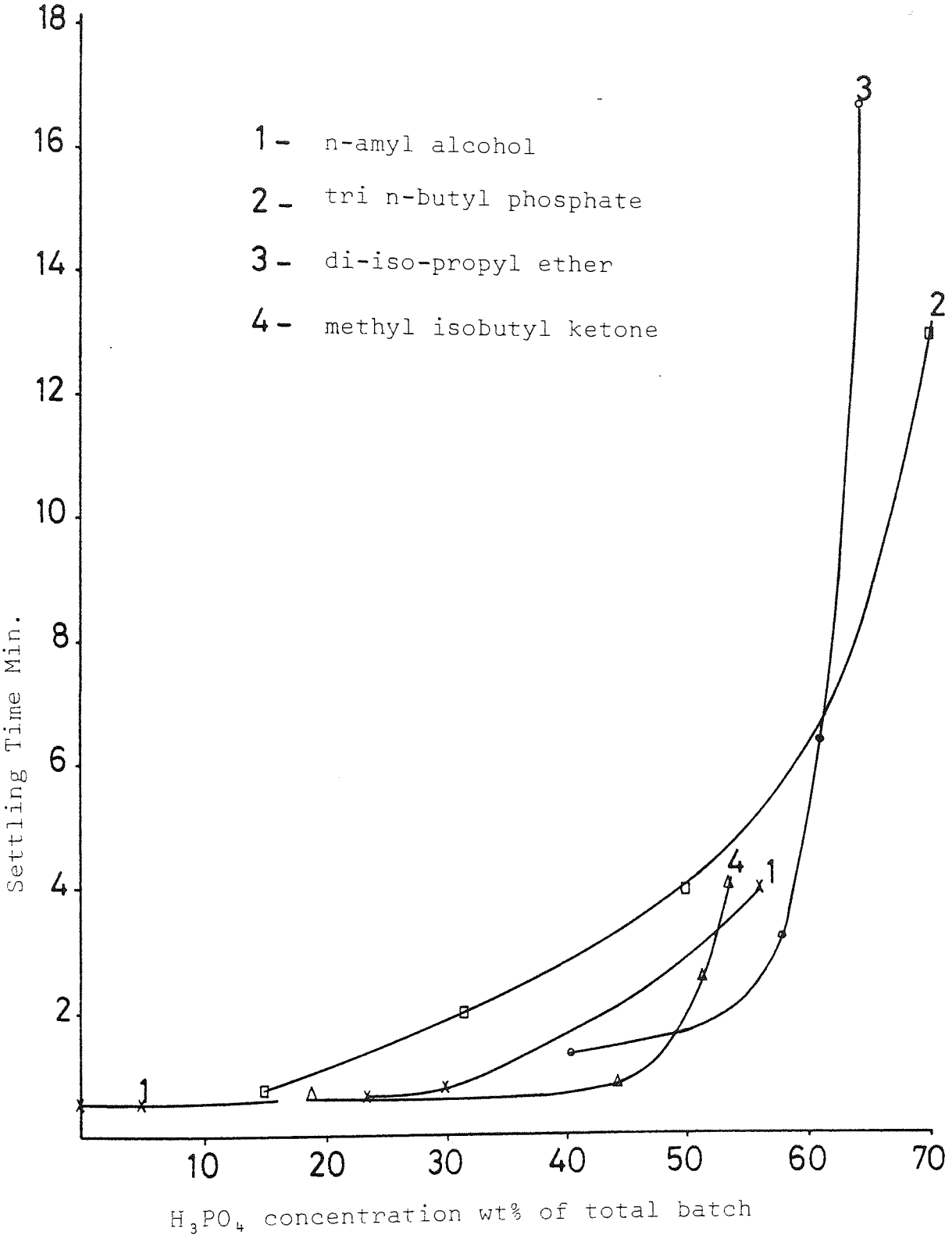


Fig.7.38 Settling time vs. H_3PO_4 concentration at 25°C, 1000 RPM
System: water - phosphoric acid - solvent
Mixtures at 1:1 by weight water to solvent (O/W)

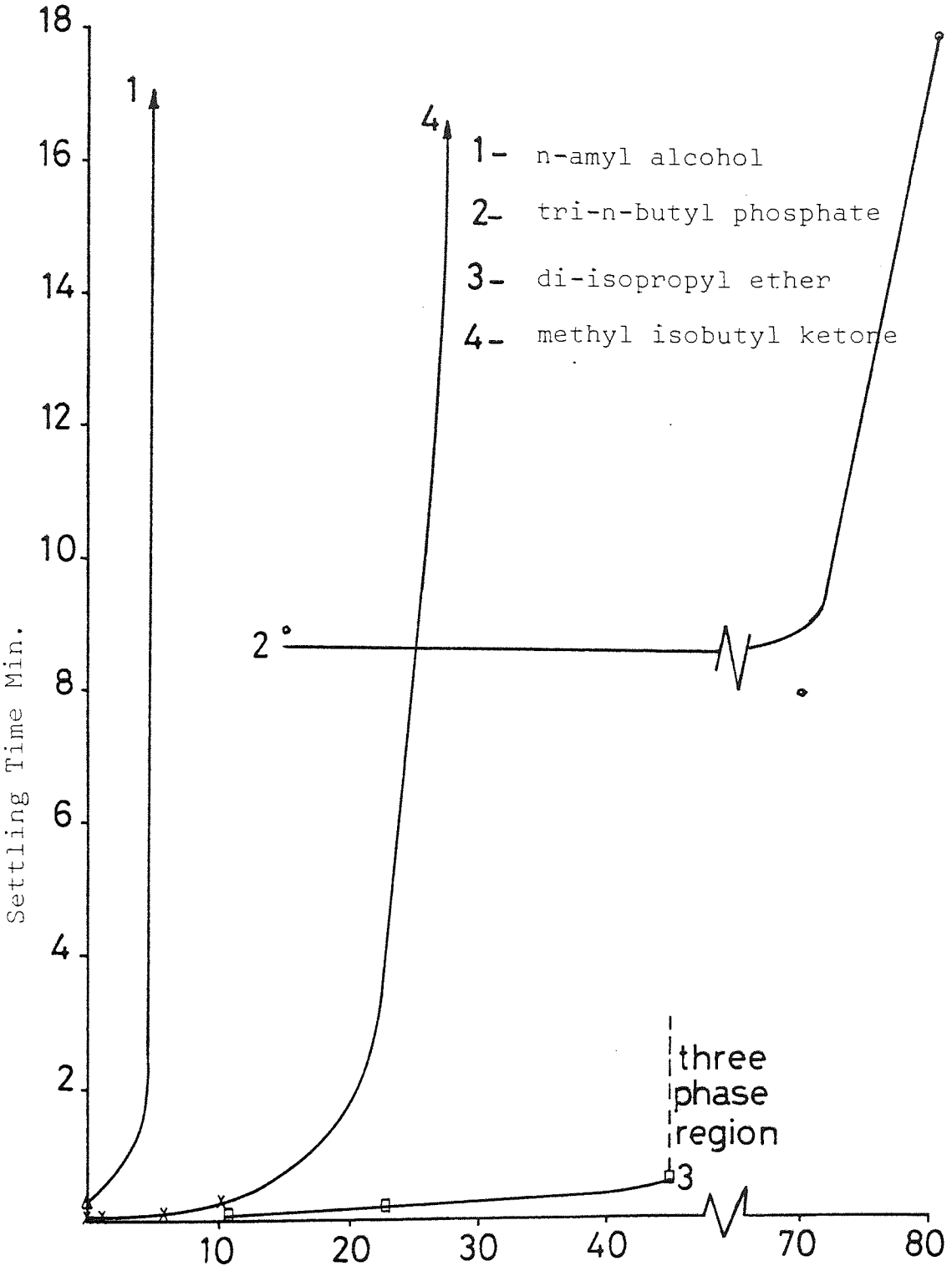


Fig.7.39 Settling time vs H_3PO_4 concentration at 25°C for mixtures of the system water - phosphoric acid - solvent at 1:1 by weight water to solvent 1000 RPM (W/O).

1- Pure system

2- With 0.5% Fe

3- With 0.3% Al

4- With 0.5% Ca or Mg

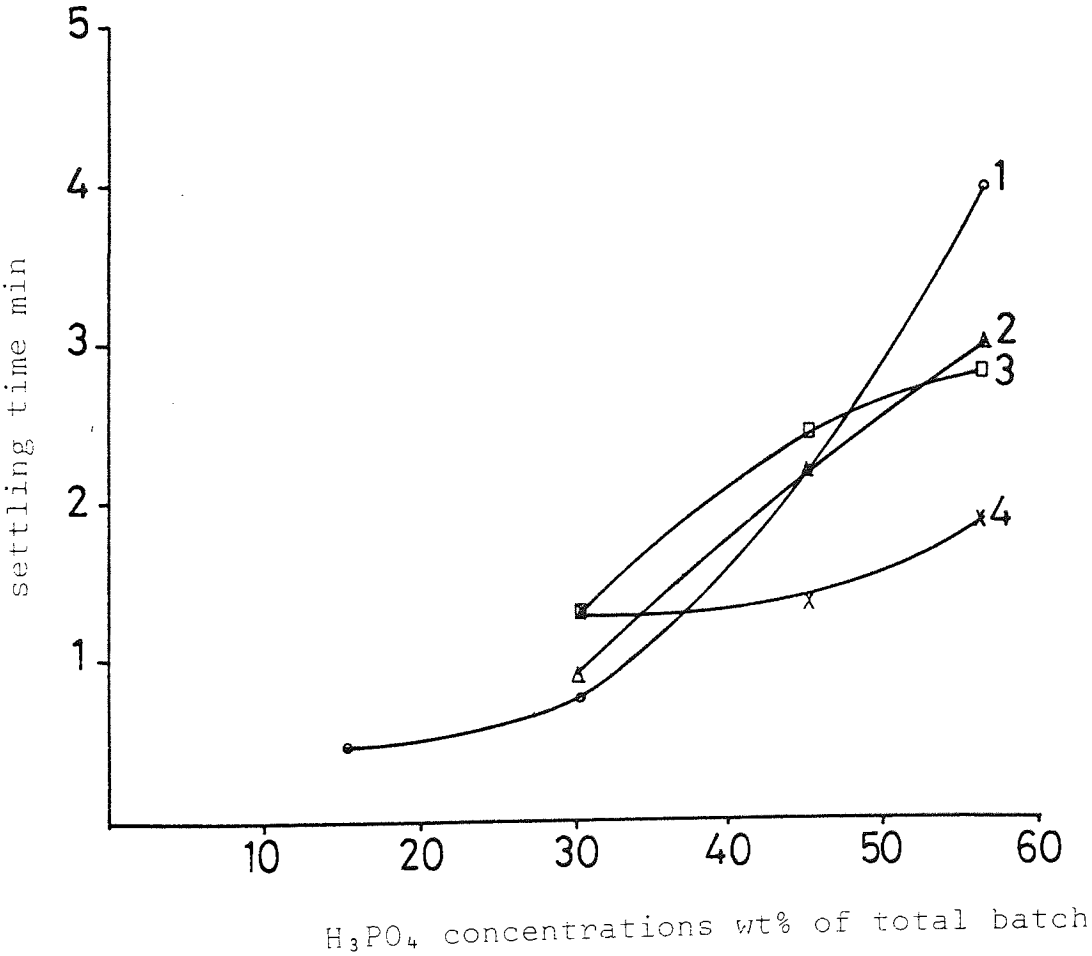


Fig.7.40 Primary break vs. H_3PO_4 concentration (effect of impurity presence on settling time).
System: water - phosphoric acid - n-amyl alcohol at 25°C. Mixtures at 1:1 by weight water to solvent, (O/W), 1000 RPM.

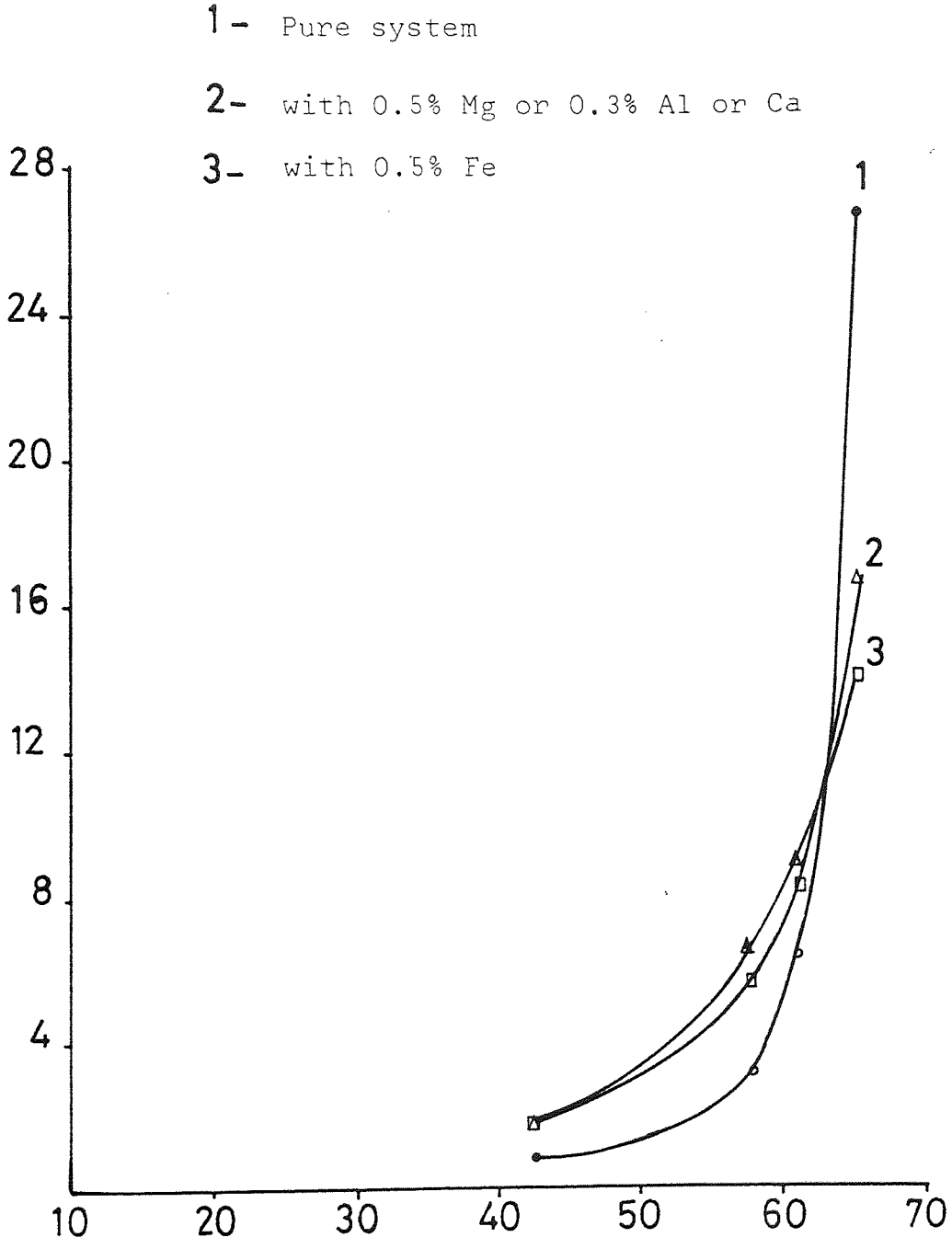


Fig.7.41 Primary break vs. H_3PO_4 concentration (effect of impurity presence on settling time). System: water - phosphoric acid - di-isopropyl ether at 25°C. Mixtures at 1:1 by weight water to solvent, (O/W), 1000 RPM.

1- Pure system

2- with 0.5% Fe, Ca or Mg 0.3% Al

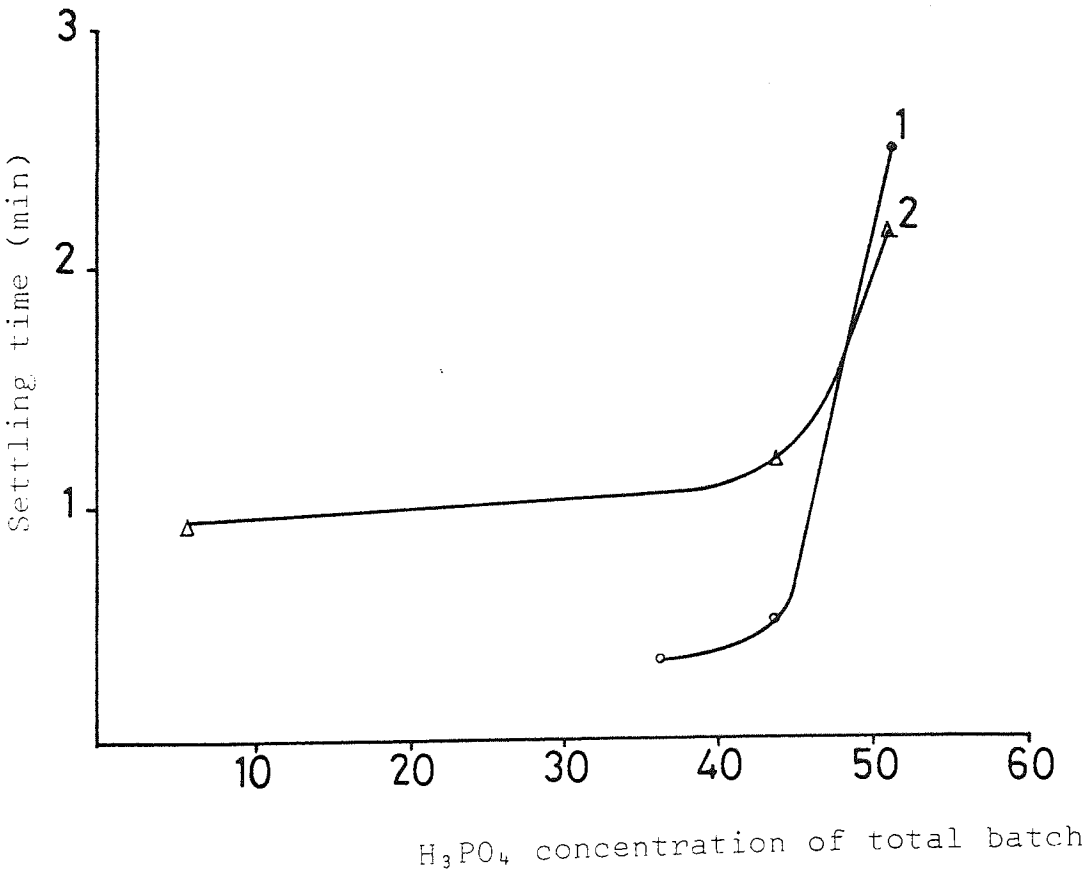


Fig.7.42 Primary break vs. H_3PO_4 concentration. System: water - phosphoric acid - methyl isobutyl ketone at 25°C. Mixtures at 1:1 by weight water to solvent, (O/W), 1000 RPM.

1- 30% H_3PO_4 of total batch (alcohol)

2- 45% H_3PO_4 of total batch (alcohol)

3- 56% H_3PO_4 of total batch (alcohol)

4- 44% H_3PO_4 of total batch (MIBK)

5- 51.2% H_3PO_4 of total batch (MIBK)

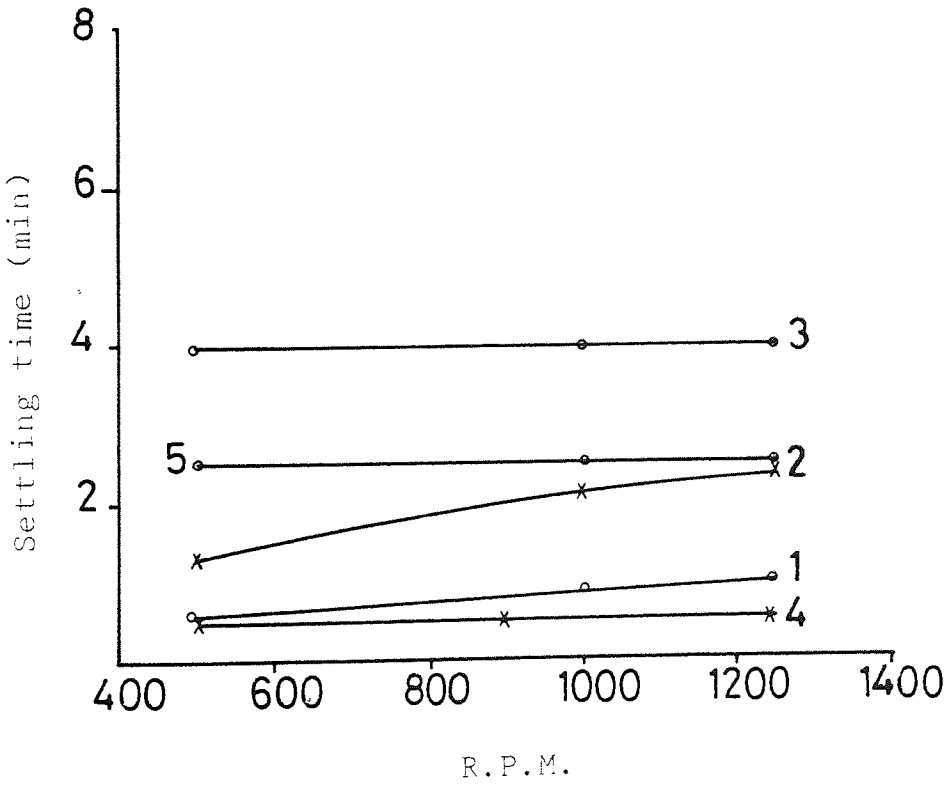


Fig.7.43 Settling time vs. RPM at 25°C for water - phosphoric acid - solvent mixtures at 1:1 by weight water to solvent, (O/W).

1- 58% H_3PO_4 of total batch

2- 61% H_3PO_4 of total batch

3- 65% H_3PO_4 of total batch

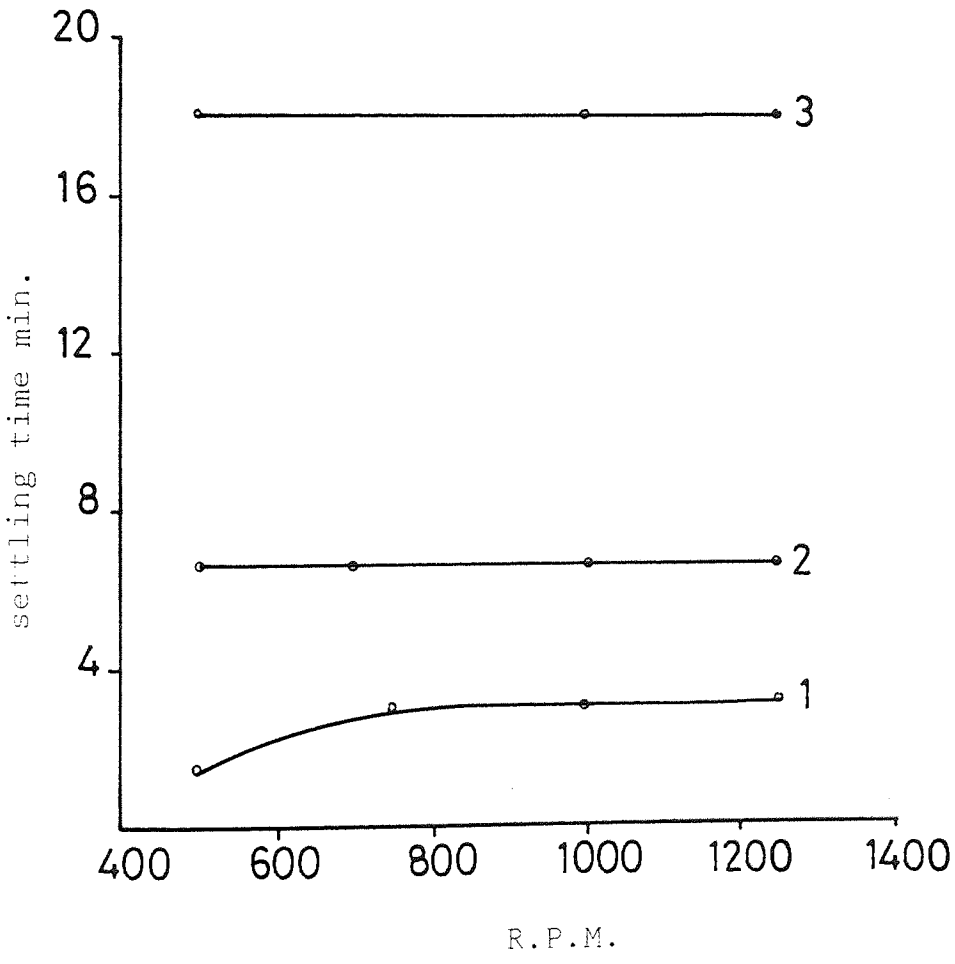


Fig.7.44 Primary break vs. RPM at 25°C for water - phosphoric acid - di-isopropyl ether mixtures at 1:1 by weight water to solvent, (O/W).

1- 15% H_3PO_4 of total batch (O/W)

2- 30% H_3PO_4 of total batch (O/W)

3- 50% H_3PO_4 of total batch (O/W)

4- 70% H_3PO_4 of total batch (W/O)

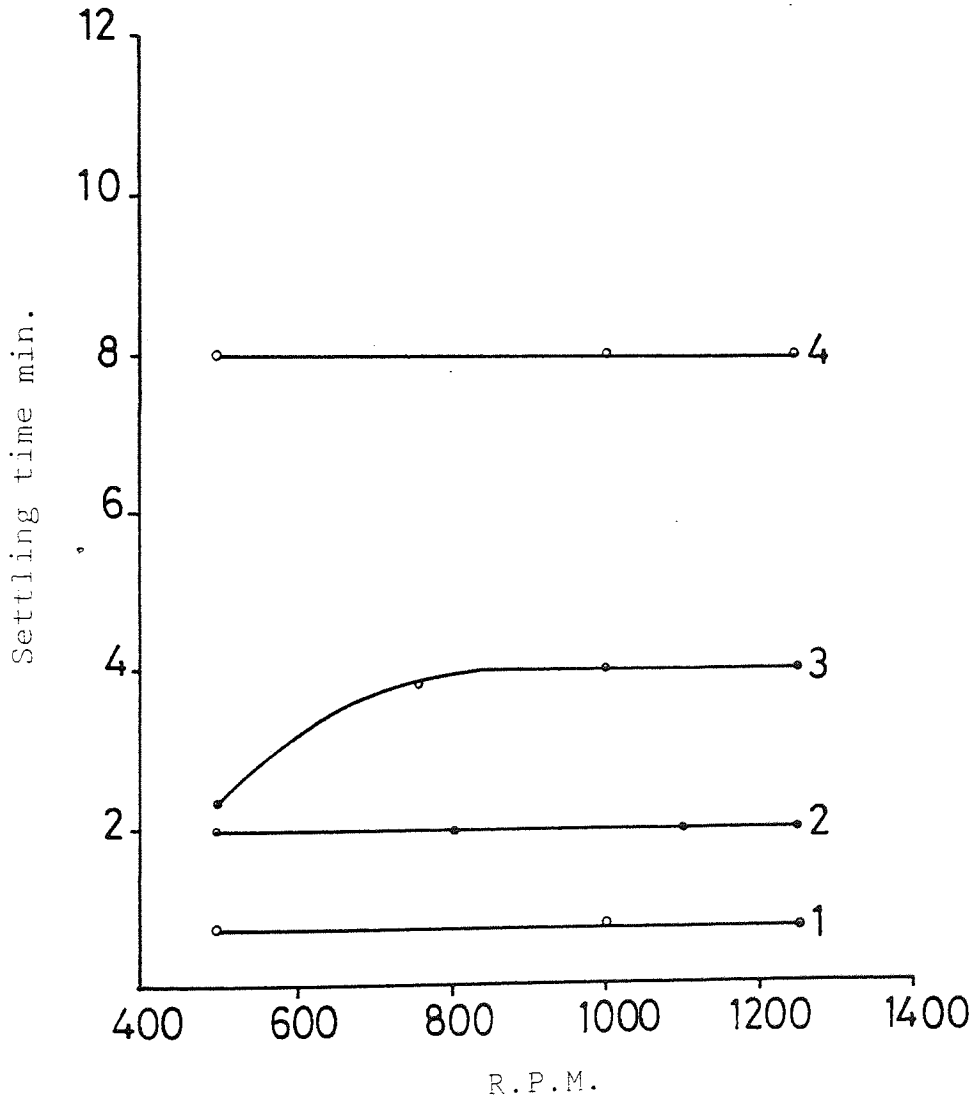


Fig.7.45 Primary break vs. RPM at 25°C for water - phosphoric acid - tri-n-butyl phosphate mixtures at 1:1 by weight water to solvent.

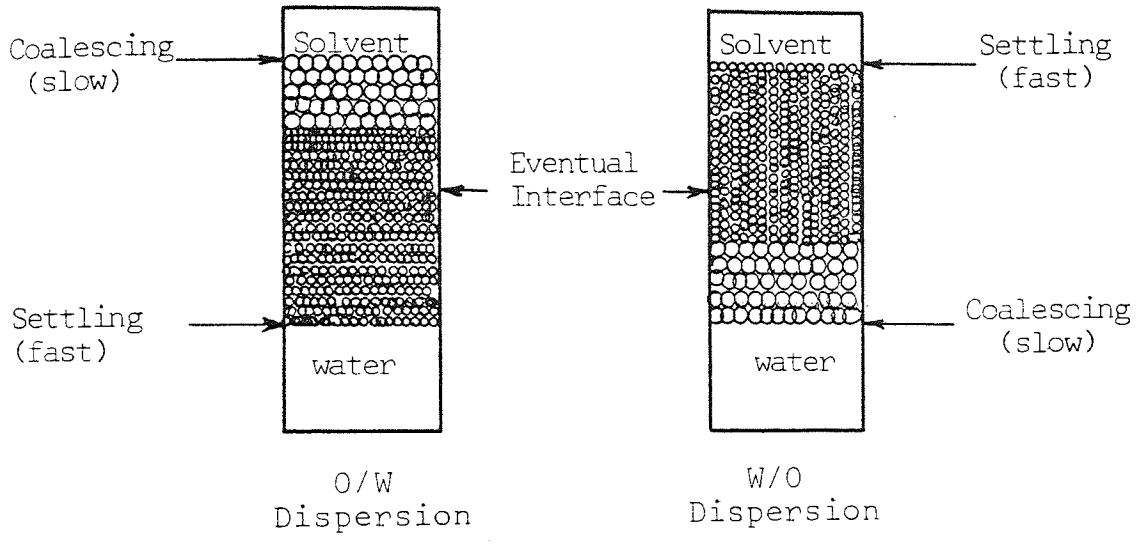


Fig.7.46 Illustration of types of dispersion

7.3 TIME TO REACH STEADY STATE

The time required to reach steady state (equilibrium in the case of a batch operation) was studied for all solvents at one acid concentration and is summarised in Figure 7.47. The results were expressed in terms of time vs. H_3PO_4 concentrations in the extract phase rather than in the raffinate phase since the change in extract acid concentration is more appreciable at the selected starting H_3PO_4 concentration. The presence of Fe in methyl iso butyl ketone did not affect the time required but affected the equilibrium H_3PO_4 concentration for reasons mentioned earlier.

7.4 EFFECT OF H_3PO_4 CONCENTRATION ON THE PHYSICAL PROPERTIES OF THE PHASES

7.4.1 Interfacial Tension

The affect of H_3PO_4 concentration on the interfacial tension for the four systems is shown in Figure 7.48. As the acid concentration increased the interfacial tension decreased and at relatively high acid concentrations the interfacial tension almost disappeared. The rate of decrease of the interfacial tension with H_3PO_4 concentration varied with the solvent and it was in the order di-isopropyl ether > methylisobutyl ketone > amyl alcohol > tri-n-butyl phosphate.

7.4.2 Specific Gravity

The specific gravity of the aqueous and extract phases for the four systems at different H_3PO_4 concentrations is summarised in Figure 7.49. The specific gravity of all the phases increased almost linearly with increase of H_3PO_4 concentration.

7.4.3 Viscosity

The viscosity of the various phases at different H_3PO_4 concentrations is shown in Figure 7.50. All curves except No. 5 were constructed from a knowledge of two viscosity valves (at the ends) for each solvent. The effect of H_3PO_4 on the viscosity of these solutions was assumed to be similar to that for the aqueous phase (No. 5) for which viscosity values were taken from reference (183).

7.5 SOLVENT STABILITY

None of the solvents studied here showed any sign of deterioration when analysed by Gas Liquid Chromotography. Only two peaks were observed in each case, one representing water and the other representing the solvent. Phosphoric acid was not picked up by the detector (Katherometer) because of its high boiling point.

However, this can not be considered a conclusive measure of the stability of the solvents, because they were only

handled at temperatures at or below 25°C. · In real practice part of the solvent may undergo some high temperature treatment in the product concentration and raffinate treatment steps, where the solvent recovered is recycled in the process. Samples of the chromotographs, with the operating conditions of the equipment are given in Appendix (IX).

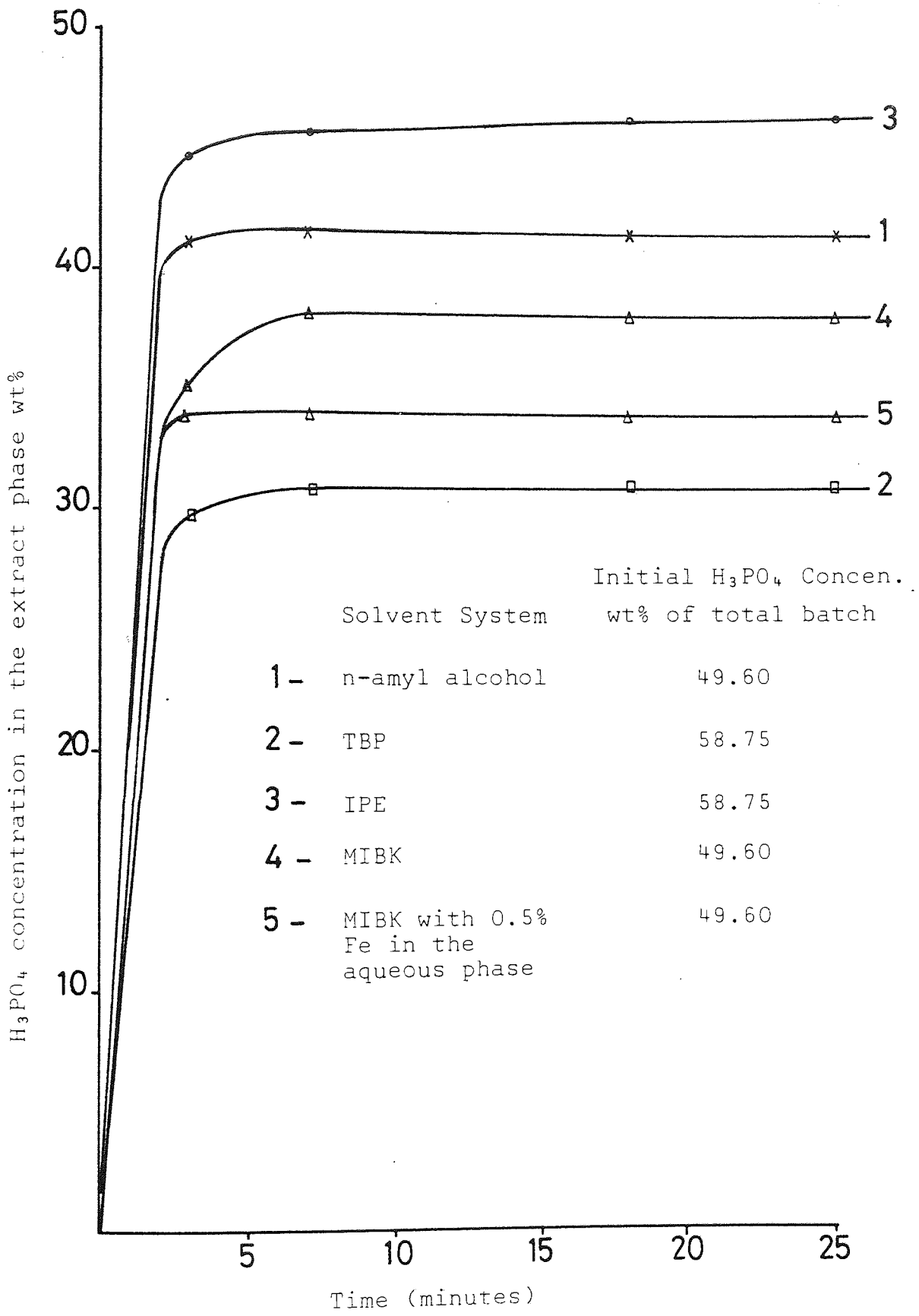


Fig.7.47 Time vs. H_3PO_4 concentration in the extract "Time to reach steady state" for water - phosphoric acid - solvent mixtures at 1:1 water to solvent at 25°C, 1200 RPM.

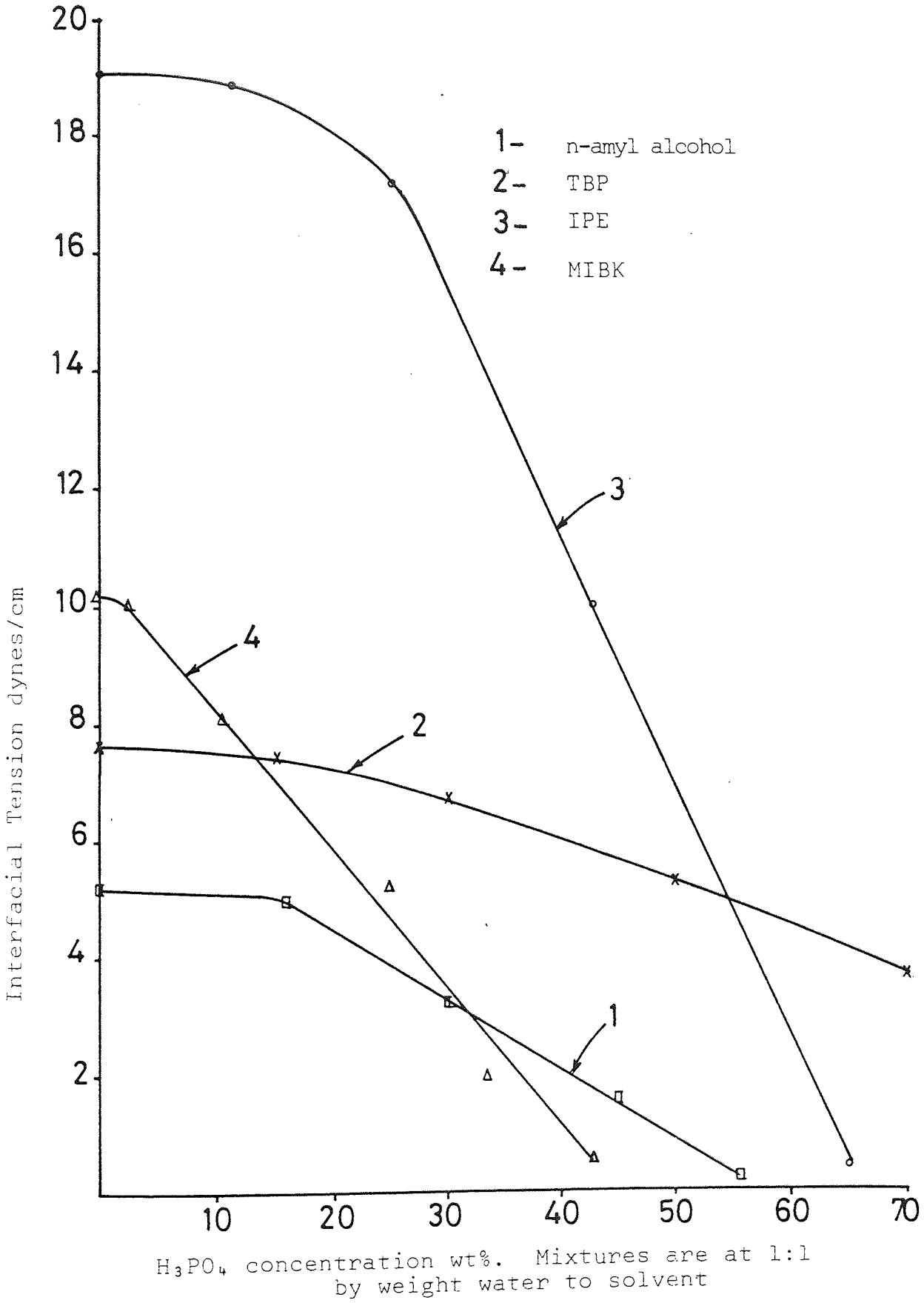


Fig.7.48 Interfacial tension for co-existing phases at equilibrium at 25°C for water - phosphoric acid - solvent.

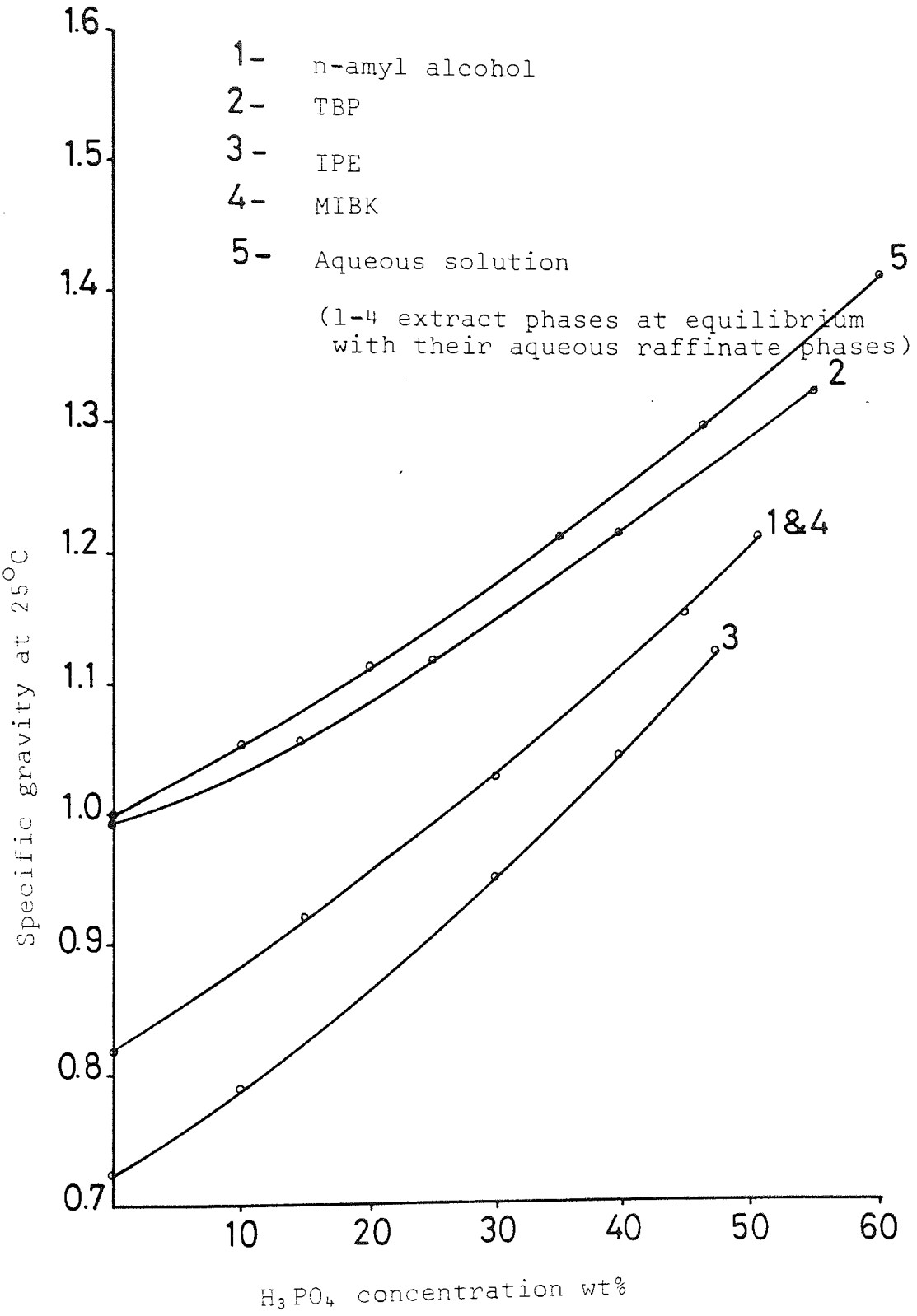


Fig.7.49 Specific gravity vs. H_3PO_4 concentration at 25°C

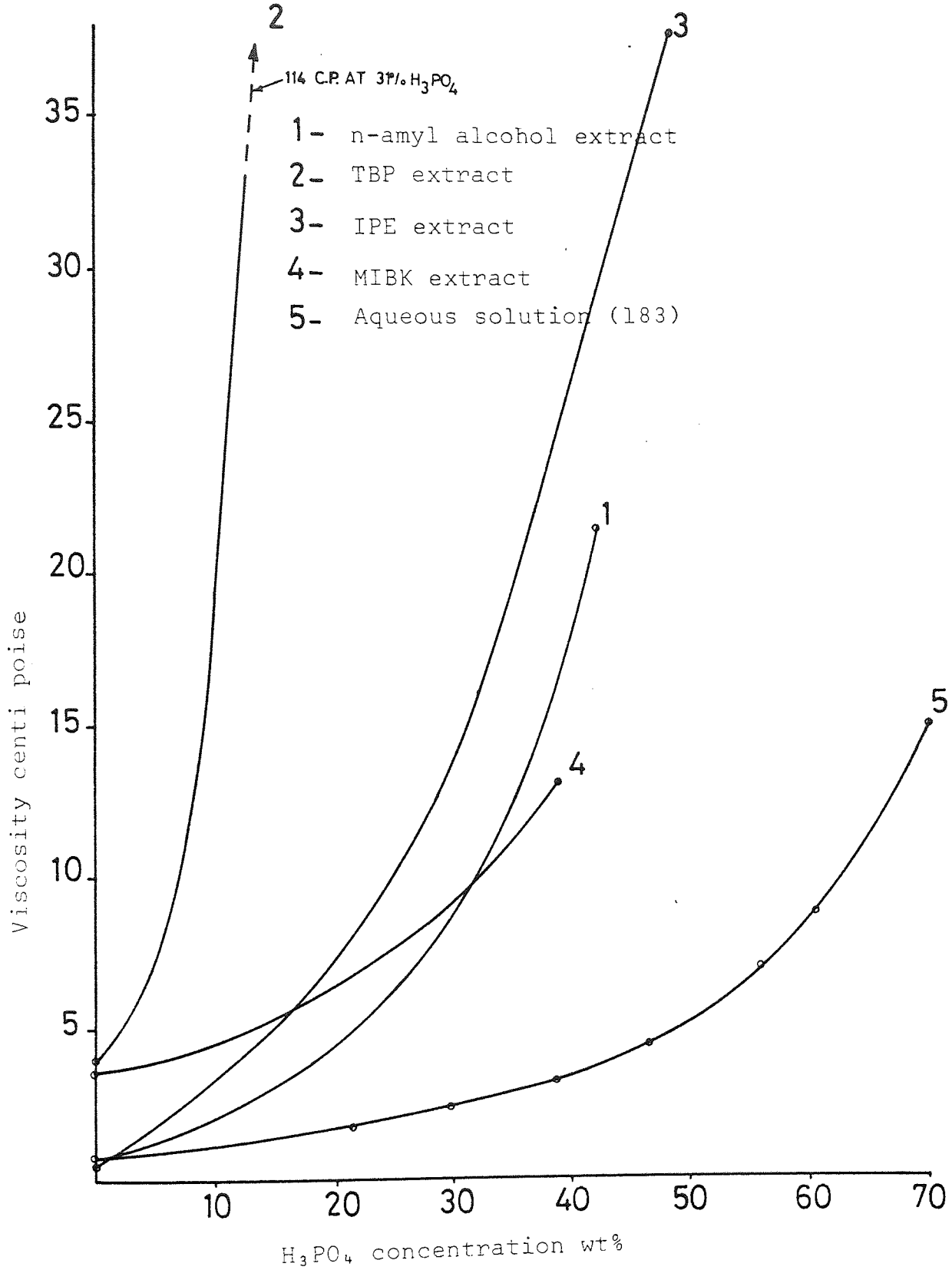


Fig.7.50 Viscosity vs. H_3PO_4 concentration at $25^{\circ}C$

(1-4 Extract phases at equilibrium with aqueous raffinate phases)

CHAPTER EIGHT

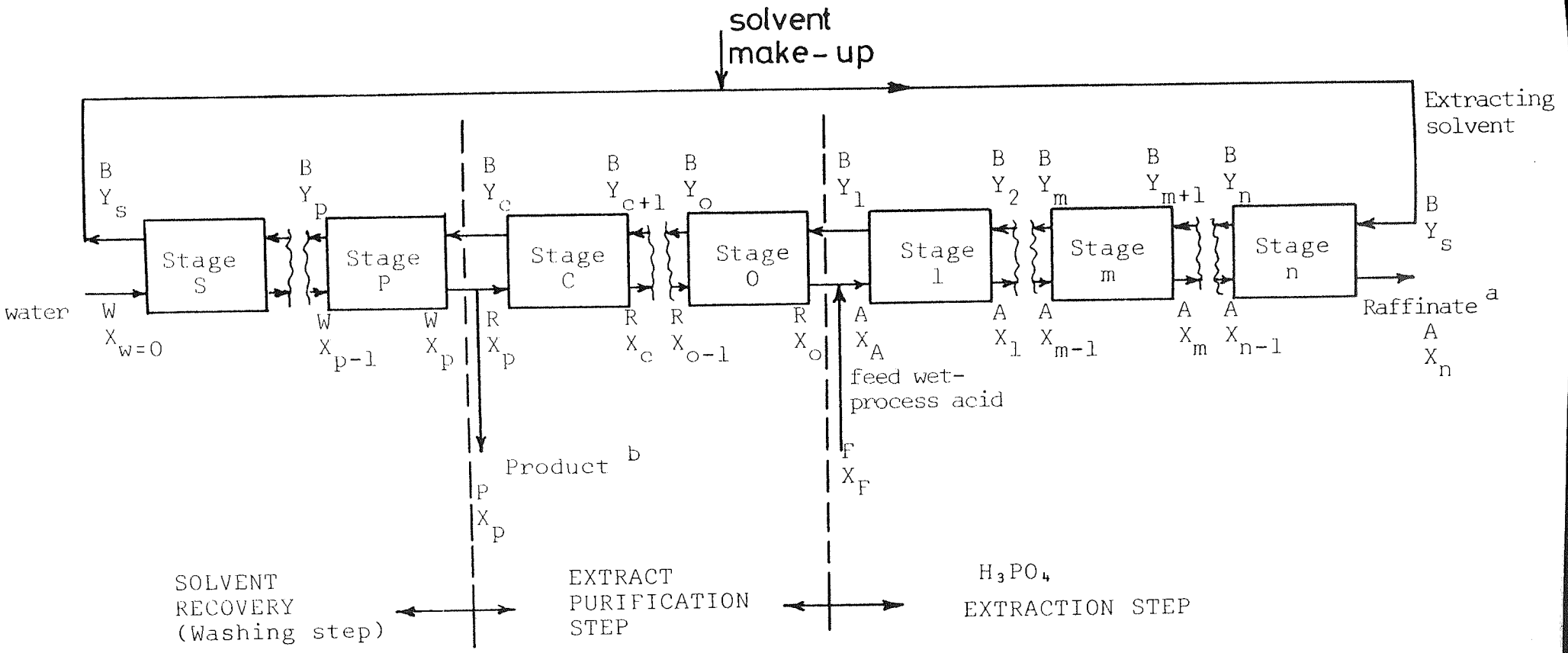
ECONOMIC EVALUATION

As mentioned earlier in Chapter 5, the objective of the process optimization was to minimize the total manufacturing cost on a plant to purify a given quality wet-process acid at a fixed P_2O_5 flow rate and quality of product using four solvents separately. The flow-sheet was outlined in figure 5.1. For the calculation of each stream flow rate the determination of the number of contact stages for the various liquid extraction steps is necessary.

8.1 CALCULATION OF THE NUMBER OF STAGES

The solvent extraction steps: phosphoric acid extraction; extract purification and enriching; and solvent recovery, can be assembled as shown in figure 8.1, and the determination of the number of stages can be carried out for each step separately.

Assuming that the solvent used was immiscible with water, the flow rates were expressed in tons/day on a solute free basis, and the solute concentrations as tons of solute per ton of carrier solvent. The number of stages for the three solvent extraction steps were calculated as follows:



(a) Product transferred to concentration section

(b) Raffinate transferred to stripping section

Fig.8.1 Detailed flowsheet of the solvent extraction steps in the purification of phosphoric acid

(i) Extraction Step:

A material balance from stage m+1 to n is

$$A.X_m + B.Y_s = A.X_n + B.Y_{m+1} \qquad (8.1)$$

From the distribution curves of H_3PO_4 shown in figure 7.26, the following relationship for the H_3PO_4 concentrations in the extract and raffinate phases can be obtained:

$$Y_{m+1} = m.X_{m+1} + b \qquad (8.2)$$

Where m is the slope of the distribution line and b is its intercept.

Setting $\varepsilon = m\frac{B}{A}$ equation (8.2) can be rearranged

$$\frac{X_m}{\varepsilon} + \frac{Y_s}{m} = \frac{X_n}{\varepsilon} + X_{m+1} + \frac{b}{m}$$

or

$$\frac{X_m}{\varepsilon} + \frac{Y_s - b}{m} = \frac{X_n}{\varepsilon} + X_{m+1} \qquad (8.3)$$

This is a first order, linear finite difference equation whose solution is

For $\varepsilon \neq 1$

$$X_m = \left(X_A - \frac{(Y_s - b)/m - X_n/\varepsilon}{1 - 1/\varepsilon}\right)\left(\frac{1}{\varepsilon}\right)^m + \frac{(Y_s - b)/m - X_n/\varepsilon}{1 - 1/\varepsilon}$$

(8.4)

Letting m = n and rearranging

$$\frac{X_A - X_N}{X_A - (Y_s - b)/m} = \frac{\varepsilon^{n+1} - \varepsilon}{\varepsilon^{n+1} - 1} \qquad (8.5)$$

$$n = \frac{\log\left\{\left(\frac{X_A - (Y_s - b)/m}{X_n - (Y_s - b)/m}\right)(1 - 1/\varepsilon) + \frac{1}{\varepsilon}\right\}}{\log\varepsilon} \qquad (8.6)$$

Equation (8.6) is a modified form of the well known Kremser-Brown-Souders equation (17) which is applied when

$$Y_m = mX_m \qquad (8.7)$$

where

$$n = \frac{\log\left\{\left(\frac{X_A - Y_s/m}{X_n - Y_s/m}\right)(1 - 1/\varepsilon) + \frac{1}{\varepsilon}\right\}}{\log\varepsilon} \qquad (8.8)$$

(ii) Purification Step:

The number of stages for the purification is calculated from a knowledge of impurity concentration in the initial extract (C_{iYl}), final extract (C_{iYc}) and recycle aqueous stream (C_{iXp}) (having H_3PO_4 concentration Y_l, Y_c and X_p respectively), distribution coefficients of the impurity (m_i) (from figures 7.17 to 7.21) and phase ratio (K_p). The distribution curve of the

impurities studied was generally found to be a straight line and could be described by equation (8.7). Accordingly a similar form to equation (8.8) can be applied to determine the number of stages.

(iii) Solvent Recovery Step:

The number of stages for this step was calculated in the same way as mentioned above. In all systems studied the acid favoured the aqueous phase especially at low concentrations, below a certain threshold in some cases as shown in the phase equilibrium diagrams.

8.2 FLOW-SHEET MATERIAL BALANCE CALCULATIONS

The concentration and raffinate treatment steps are not included in the material balance. With reference to figure 8.1.

1 - Overall Material Balance

(i) Total material balance

$$F + W = A + P \qquad (8.9)$$

(ii) H_3PO_4 Balance

$$F \cdot X_F + 0 = A.X_n + P.X_p \qquad (8.10)$$

2 - Extraction Step Material Balance

(i) Total material balance

$$F + R + B = A + B$$

$$\therefore \quad A = F + R \qquad (8.11)$$

(ii) H_3PO_4 balance

$$F.X_F + R.X_o + B.Y_s = A.X_n + B.Y_1 \qquad (8.12)$$

$$Y_1 = \frac{1}{B}(F.X_F + R.X_o - A.X_n) + Y_s \qquad (8.13)$$

$$= \frac{A}{B}\left\{\frac{F.X_F + R.X_o}{A} - X_n\right\} + Y_s$$

letting

$$\frac{B}{A} = R_E$$

$$Y_1 = \frac{1}{R_E}\left\{\frac{F.X_F + R.X_o}{A} - X_n\right\} + Y_s$$

3 - Purification Step

(i) Total material balance

$$R + B = R + B$$

(ii) H_3PO_4 balance

$$R.X_p + B.Y_1 = R.X_o + B.Y_c$$

$$X_o = \frac{B}{R}(Y_1 - Y_c) + X_p \qquad (8.14)$$

The phase ratio for the purification section K_p is defined as

$$K_p = \frac{R \,.\, (X_p + 1)}{B \,.\, (Y_1 + 1)}$$

or

$$R = K_p \,.\, B \,\frac{(Y_1+1)}{(X_p+1)} \qquad (8.15)$$

Substituting equation (8.15) in equation (8.14)

$$X_o = \frac{X_p + 1}{K_p(Y_1+1)} (Y_1 - Y_c) + X_p$$

or

$$Y_c = Y_1 - K_p(X_o - X_p) \frac{Y_1+1}{X_p+1} \qquad (8.16)$$

4 - Solvent recovery step

(i) Total material balance

$$B + W = B + W$$

(ii) H_3PO_4 balance

$$B.Y_c + 0 = B.Y_s + W.X_p$$

$$W = \frac{B(Y_c - Y_s)}{X_p} \qquad (8.17)$$

but

$$W = P + R = P + K_p \cdot \frac{B(Y_1 + 1)}{X_p + 1} \qquad (8.18)$$

rearranging equations (8.17) and (8.18)

$$B = P/\left\{ \frac{(Y_c - Y_s)}{X_p} - \frac{K_p(Y_1 + 1)}{X_p + 1} \right\} \qquad (8.19)$$

where P is known.

In equation (8.19) Y_c and Y_1 are as yet unknown, but can be determined from the calculation of the number of stages for the purification step (n_p) as follows:

$$n_p = \frac{\log\left\{\frac{(C_{iy_1} - C_{ixp}/m_i)}{C_{iy_c} - C_{ixp}/m_i}\left(1 - \frac{1}{m_i K_p}\right) + \frac{1}{m_i K_p}\right\}}{\log m_i K_p} \qquad (8.20)$$

where n_p is also defined as

$$n_p = \frac{\log\left\{\frac{X_p - (Y_1 - b)/m}{X_o - (Y_1 - b)/m}\left(1 - \frac{1}{\varepsilon_1}\right) + \frac{1}{\varepsilon_1}\right\}}{\log \varepsilon_1} \qquad (8.21)$$

where $\varepsilon_1 = m \times \frac{R}{B}$.

Rearranging equation (8.21)

$$X_o = X_p - \left(X_p - \frac{Y_1 - b}{m}\right) \cdot \frac{\varepsilon_1^{n+1} - \varepsilon_1}{\varepsilon_1^{n+1} - 1} \qquad (8.22)$$

but the value of Y_1 is unknown, and another equation is needed. From equation (8.13)

$$Y_1 = \frac{1}{B}\left\{(A-R)X_F + R.X_o - A.X_n\right\} + Y_s$$

or

$$Y_1 = \frac{1}{B}\left(R(X_o - X_F) + A(X_F - X_n)\right) + Y_s \qquad (8.23)$$

Substituting equation (8.15) in equation (8.23)

$$Y_1 = \frac{K_p(Y_1+1)(X_o-X_F)}{X_p + 1} + \frac{A}{B}(X_F-X_n) + Y_s$$

or

$$Y_1 = \frac{K_p(X_o-X_F) + (\frac{1}{R_E}(X_F-X_n)+Y_s)(X_p+1)}{X_p + 1 - K_p(X_o-X_F)} \qquad (8.24)$$

Solving equations (8.22) and (8.24) simultaneously will evaluate X_o and Y_1 at any given X_F, X_n, X_p, Y_s, R_E and K_p.

Using equation (8.16), Y_c can be calculated
equation (8.19), B can be calculated, and then
all other streams.

N.B. In the general case of solvent extraction process with reflux, n_p cannot be determined analytically. However, it can be treated as a variable subject to optimization as are the other variables (X_n, Y_s, R_E and K_p).

8.3 MANUFACTURING COST EVALUATION

Considering that the nature of the solvent, the type of extractor, the amount of product and its concentration and the concentration of feed are fixed, the flow rate and concentration can be evaluated for each stream. The total annual manufacturing cost (C_T) can be taken as the sum of seven costs as defined in Section 5.2.1.

$$C_T = I + II + III + IV + V + VI + VII$$

I - Annual Cost of Extraction Step

$$I = \frac{n_E C_E}{E_{OE}}$$

where

$$n_E = \frac{\log \left\{ \frac{X_A-(Y_s-b)/m_E}{X_n-(Y_s-b)/m_E} \left(1-\frac{1}{m_E R_E}\right) + \frac{1}{m_E R_E} \right\}}{\log m_E R_E}$$

The annual cost per stage (C_E) is given by

$$C_E = C_{VE}\left(\frac{p}{y}+b^*\right)_E + (P_A+P_p)W.H$$

C_{VE} includes the purchase cost of Mixer-Settler equipment, (including agitating equipment and two pumps per stage) as described in Appendix (V).

p is 1.0 + The cost of instruments, piping and installation, as fraction of the major equipment cost, so that $C_{VE}.p$ is the installation cost per stage.

y is the pay out time, b* allows for maintenance, and P_A+P_p is the power requirement for agitator and pump.

W is the cost of power, and H the hours of operation per year.

E_{OE} overall stage efficiency for the extraction step. This was assumed to be constant (0.9) as were the efficiencies of other solvent extraction steps.

II - Annual Cost of Raffinate Lost Value and Treatment

This was calculated from a proposed relationship

$$II = A.X_n.L$$

Where A and X_n are the raffinate flow rate and H_3PO_4 concentration. L is £ per ton loss in value and treatment of the raffinate phase because it is richer in impurities and lower in H_3PO_4 concentration than the feed wet-process acid.

III - Annual Cost of Purification Step

$$III = \frac{n_p C_p}{E_{Op}}$$

The cost is calculated in a similar way to item I.

IV - Annual Cost of Solvent Recovery Step

Since the solvent recovery from the purified extract is carried out by a solvent extraction process using water to extract the H_3PO_4 , this item was calculated similarly to items I and III as follows:

$$IV = \frac{n_W C_W}{E_{OW}}$$

where

$$n_W = \frac{\log\left\{\frac{Y_C}{Y_s}\left(1 - \frac{1}{m_W R_W}\right) + \frac{1}{m_W R_W}\right\}}{\log m_W R_W}$$

V - Annual Cost of Solvent Losses

The cost of solvent losses was calculated from the relationship

$$V = \left\{ \frac{n_E}{E_{OE}} + \frac{n_P}{E_{OP}} + \frac{n_W}{E_{OW}} \right\} \quad B.\ell.S.H.$$

where ℓ is the fraction of solvent flow lost per stage,

S value of solvent. £/ton

VI - Annual Cost of Concentration of Product Acid

Ideally the product acid should have the same H_3PO_4 concentration as the feed acid without the need for thermal concentration. When this was not possible, the additional cost was calculated as follows:

$$VI = P.(1+X_p).(X_F-X_P).C_P$$

where C_P is the cost of concentrating one ton of acid by 1% H_3PO_4, £.

VII - Annual Labour Cost

This was considered to be constant irrespective of the flow-sheet. Two men per shift at £4000/year, 3 shifts per day were assumed.

VII = 2 x 3 x 4000

= £24000

8.4 OPTIMIZATION COMPUTATION PROGRAM

The computer program was written in the Fortran IV language and run in an ICL 1904 Computer. The list of the program and the results obtained are reproduced in Appendix (X). The program consisted of the following parts -

1. Master, inputs data, arrange for parameter testing and print the results.
2. Subroutine POWELL, defines all the variables and constants and performs the optimization procedure laid down in Section 5.2.2.4.
3. Subroutine CAMPEY, finds the optima along a defined direction as described in Section 5.2.2.5.
4. Subroutine YVALUE, evaluates the flowsheet material balance and finds the total annual manufacturing cost.

The above parts are related to each other in the manner shown in Figure 8.2.

The results obtained in Appendix (X) were based on a plant producing 100 tons/day P_2O_5 product. These are tabulated in the following order; data, parameters and starting values of the independent variables for the four systems, then starting with di-isopropyl ether, the calculated optimum values for the independent variables and parameters, the number of stages

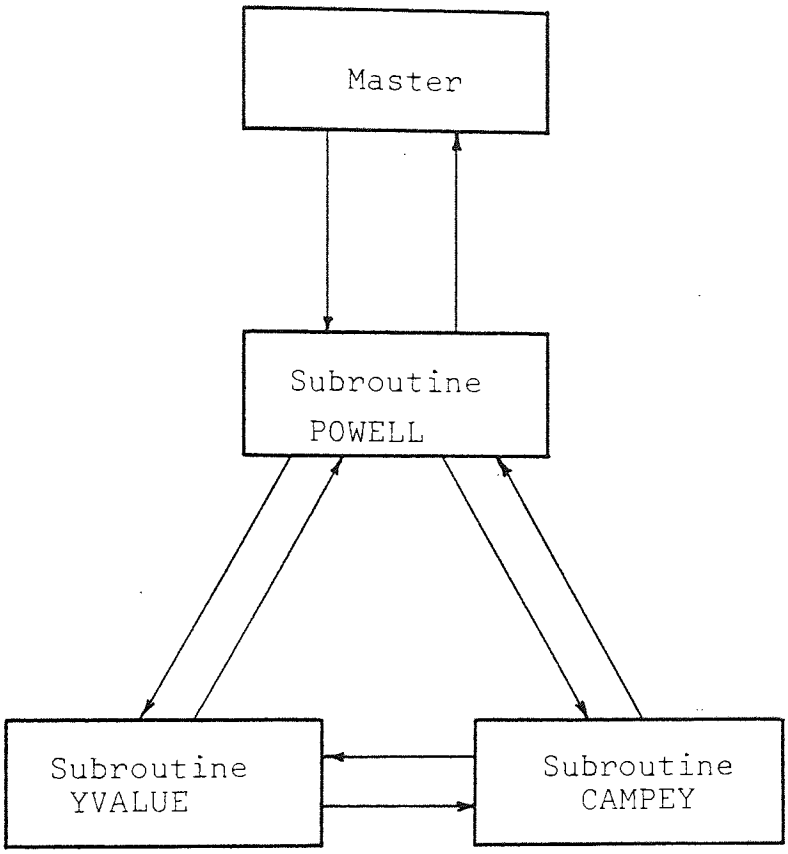


Fig.8.2 General inter-relationship of the various parts of the computation program.

required for the three solvent extraction steps, the flow-sheet flow rates and concentrations and the individual step costs and final cost. These were tabulated including a case number for each set of tested parameters (Y_s, X_p, ℓ% loss and C_{iYl}). The symbols have the same meanings as defined earlier in Chapter 5.

Subroutines POWELL and CAMPEY were programmed to perform either maximization or minimization of any defined objective function in subroutine YVALUE. The following controls have to be defined by the user:

1. M2, if -1, the program will minimize the objective function and if +1 will maximize it.
2. IP, if greater than 1, details of the various optimization steps will be printed.
3. N, the number of independent variables.
4. AQ the required accuracy tolerance between two adjacent points at the optimum.
5. S, the starting step length for successive changes in the independent variables to find the optima along a defined direction.

CHAPTER NINE

DISCUSSION

9.1 EXPERIMENTAL RESULTS

9.1.1 Phase Equilibrium Studies

A. Phosphoric Acid

The proportion of the three phase diagram representing a heterogeneous system for the four systems, water-phosphoric acid - solvent, studied was approximately as follows: 64.5% with n-amyl alcohol and methyl isobutyl ketone, 76.5% with di-iso-propyl ether and 89.3% with tri-n-butyl phosphate. The presence of impurities increased this area by roughly 5% except in the case of tri-n-butyl phosphate, where less than 1% increase was observed.

It was not possible to operate with aqueous solutions containing higher than 72% H_3PO_4 (52.2% P_2O_5) using n-amyl alcohol and methyl iso butyl ketone, since the two phases became miscible in almost any proportion.

About 1-2% of solvent was always present in the aqueous phase for all systems except tri-n-butyl phosphate where only trace amounts were present. Apart from the need to remove this solvent from the product it is ncessary to reover it and recycle it to avoid economic loss.

The sharp decrease in the distribution coefficient of phosphoric acid at concentrations below a certain threshold level placed a limit on the amount of phosphoric acid extractable from the feed. For any practical extraction, the acid concentration of the feed (normally 75% H_3PO_4) could only be reduced in the raffinate to 68% H_3PO_4 with di-iso propyl ether and 55% H_3PO_4 with methyl-iso-butyl ketone. This meant that a high proportion of phosphoric acid in the feed (roughly about 80%) was produced as impure raffinate. Nevertheless, the product acid could be recovered at relatively high H_3PO_4 concentrations.

Although it was possible to extract most of the phosphoric acid from the feed with n-amyl alcohol and tri-n-butyl phosphate, it was only practical to reduce the phosphoric acid concentration of the raffinate down to a certain level. This was due to the appreciable decrease in the phosphoric acid distribution coefficient at low acid concentrations.

Comparison between the results achieved in this work and published data on the phase equilibrium diagram of water-phosphoric acid - solvent for di-isopropyl ether (149) and n-amyl alcohol (145) showed distinct differences in both cases. The size of the heterogeneous area in both published cases was slightly smaller. Also, the three phase region was not defined or even mentioned in the case of di-isopropyl ether and it appeared to be very inefficient for the extraction of phosphoric acid.

The presence of impurities had two opposite effects on the acid extraction process. On the one hand, they lowered the slope of acid distribution curve and on the other hand they increased the mutual immiscibility of the aqueous and organic phases. This helps to increase the selectivity of the solvent towards the acid and provides the possibility of operating with a higher acid concentration. The latter phenomenon is especially beneficial for n-amyl alcohol and methyl isobutyl ketone systems.

It was observed that all tested cationic impurities had a similar effect and the extent of such effect was roughly proportional to their concentration in the feed. A relationship to express the effect of the impurities on the slope of the distribution coefficient curve and hence on the extraction operation can be made as follows: -

From Figure 9.1

$$Y_p = m_{ep} X_p + b \qquad (9.1)$$

Where m_{ep} is the slope of the distribution line and b is its intercept for the pure case

$$Y_i = m_{ei} X_i + b' \qquad (9.2)$$

Where m_{ei} and b' are the slope and intercept for the impure case.

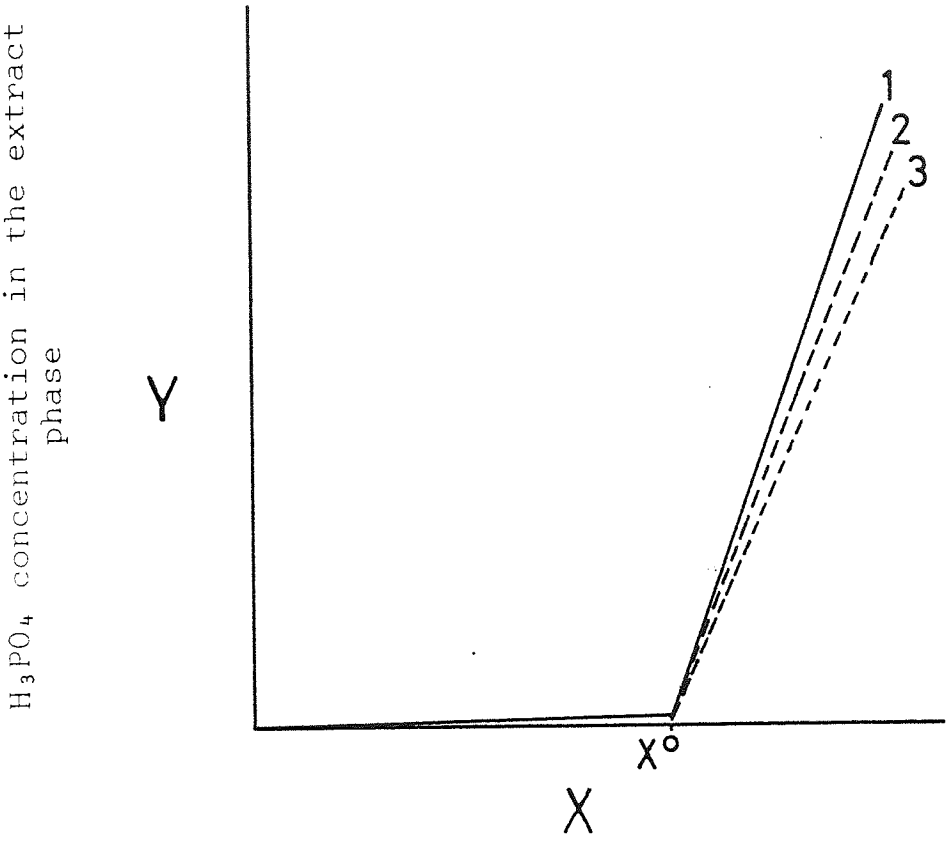


Fig.9.1 Effect of impurity presence on the slope of the distribution curve for phosphoric acid

1) In the case of pure system
2) In the presence of cationic impurities in the feed acid
3) In the case of impure system at higher concentration of soluble cationic impurities in the feed than in 2).

But

$$m_{ei} = (m_{ep} - kC_i) \qquad (9.3)$$

Where C_i is the impurity concentration and k is a constant characteristic of the impurity,

$$\therefore \qquad Y_i = (m_{ep} - kC_i)X_i + b' \qquad (9.4)$$

b' can be calculated from known information at $Y_p = Y_i = 0$ where $X_p = X_i = X^o$.

With regard to calcium, magnesium and presumably all mono or di-valent cations that can replace the strong hydrogen ion of the acid, the acid concentration of the finished raffinate was reduced because of the chemical reaction described in Appendix (III). This means a loss in the available P_2O_5 content.

B. Impurities

The effect of phosphoric acid concentration on the distribution coefficient of impurities was discouraging to a certain extent, since it increased sharply at high acid concentrations at which practical extraction operations have to be performed. Di-isopropyl ether was found to be the highest selective solvent regarding phosphoric acid followed by tri-n-butyl phosphate, methyl isobutyl ketone and n-amyl alcohol. Iron (Fe^{3+}) always had a higher distribution coefficient than the other cationic impurities followed by calcium, aluminium

and magnesium respectively.

The rise in the distribution coefficient of impurities with wet-process phosphoric acid could be attributed to the lowering in the internal pressure of the aqueous phase. However, no similar rise in the acid distribution coefficient was observed which nullifies the possibility of impurities having a salting-out effect both individually and collectively.

From what has been claimed and observed regarding the effect of cationic impurities, it may be concluded that for a salt to produce a salting out effect on a phosphoric acid extraction process, the cation must be tri-valent and its phosphate must be highly soluble in acid solutions at fairly low acid concentration. This requirement is virtually impossible to meet. A mono or di-valent salt will only succeed as a salting-out agent provided it is present in other than phosphate form and non reactive with the acid. For instance a chloride soluble in excess acid must not produce free HCl and phosphate precipitate.

Neither anionic impurities such as sulphates or fluorides nor organic impurities were tested, since rapid and accurate analysis was not achievable for the large number of systems studied. Anionic impurities, however, tend to (99, 110) increase the distribution coefficient of the acid and would be expected to have similar or slightly higher distribution coefficients themselves to cationic impurities since they are present in the form of saturated cationic salts.

9.1.2 Hydrodynamic Studies

9.1.2.1 Drop Size Distribution

The presence of phosphoric acid decreased the interfacial tension of the systems and increased the density and viscosity of the contacted phases. As a result of the drop-size of the dispersions decreased and the settling time increased. An attempt to fit the data obtained into Hinze's (32) equation was made as follows:

$$d_{max} = k_1 \left(\frac{\sigma}{\rho_c}\right)^{0.6} E^{-0.4} \qquad (9.5)$$

Where E is power per unit mass and time, and can be expressed by the formula

$$E = \frac{k_2 \, N^3 \, dp^5}{M} \qquad (9.6)$$

where

k_1 = 0.725

k_2 = 1.0 for propellers

dp = 3.0cm (propeller diameter)

M = 200gm (total weight of the batch)

Inserting these values and rearranging equation (9.5)

$$d_{max} = 0.671 \left(\frac{\sigma}{\rho_c}\right)^{0.6} N^{-1.2} \qquad (9.7)$$

Using equation (3.17)

$$d_{32} = 0.38 d_{max}$$

The results obtained from equation (9.7) were compared with the experimental values. These are shown in Appendix (VI).

1. With methyl isobutyl ketone (MIBK) and di-isopropyl ether (IPE) the deviation of the calculated from the experimental results generally increased with decreasing agitator speed, always in favour of higher calculated values. This suggested the possibility of k_1 being affected by the dynamic conditions and physical properties of the system. Relations from linear regression analysis were obtained to express the value of k_1 in terms of agitator Reynold's number (Re) and Webber number (We). These are presented in Table 9.1, where

$$k_1 = k_3 \times (Re)^a (We)^b$$

In both MIBK and IPE systems it was evident that (Re) number has the greater effect on the expected experimental value of k_1. However, when the data of both systems were combined, the (We) number showed the greater effect with the multiple correlation coefficient decreasing to 0.826. This can be explained by the difference in surface properties (expressed by interfacial tension) of the two systems, although other physical properties such as density and viscosity were similar.

TABLE 9.1 : Results of linear regression analysis to rectify the value of k_1 in equation (9.5) (Independent variables at significant level 99.00%)

System	Coefficients			Mult. Corr. Coeff.	Res. Error	E.S.S.
	k_3	a	b			
di-isopropyl ether	1.26×10^{-4}	0.829	0.004	0.938	0.1126	0.0633
methyliso-butyl ketone	2.52×10^{-2}	0.288	0.093	0.975	0.0528	0.0223
mixed data of above solvents	3.79×10^{-2}	0.048	0.398	0.826	0.1496	0.3586

Higher agitator speeds were required to disperse the phases in the case of the di-isopropyl ether system. That is to say higher (Re) numbers were studied, but not higher (We) numbers since the effect of increased agitator speed was nullified by the increased interfacial tension as follows:

$$We = \frac{N^2 D^3 \rho_c}{\sigma}$$

while

$$Re = \frac{ND^2\rho_c}{\mu}$$

Therefore, to obtain a relationship which represents the data for two systems with different interfacial tensions, the Webber number should be used and the Reynold's number ignored. Nevertheless the factors affecting the value of k_1 have to be taken separately if a reliable prediction of drop-size is required for each system.

For both solvents the expected experimental values of k_1 approached 0.8 at high Reynold's numbers. This trend agrees with the value quoted by Hinze (32). Hinze's equation (9.5) was derived for systems having high Reynold's numbers and low phase ratios where break-up is predominant. This condition however, was not fulfilled in this work.

2. With tri-n-butyl phosphate (TBP) the calculated drop-sizes were always higher than the experimental. The Reynolds number values were also relatively low. However, no clear trend

regarding its effect on the drop-size was observed. The expected experimental k_1 values oscillated about 0.47 with a maximum deviation of about $\pm$ 10%. At high H_3PO_4 concentrations, the system became appreciably viscous which might have had an effect on the drop-size behaviour.

Inadequate data regarding the n-amyl alcohol system were obtained due to unclear photographic results and therefore, no clear conclusion can be drawn.

9.1.2.2 Phase Inversion

The factors affecting which phase is to be continuous and the possibility of phase inversion at the prevailing phosphoric acid concentration were not clear. However, the conditions existing at each event could be summarised as follows:

1. At low acid concentrations (see Section 7.2), where the organic phase was the continuous phase in most cases. The volume of organic phase was normally higher than the aqueous phase and the viscosity and density as well as $\Delta\rho$ were relatively low. However, with di-isopropyl ether, the organic phase remained continuous even when its volume proportion was less than 45%. The ρ_{aq} was about 1.5 and $\Delta\rho$ about 0.65 with similar changes in the aqueous phase viscosity.

2. With increasing acid concentration (medium range), the volumes of the phases were similar, and viscosities, densities

as well as $\Delta\rho$ increased accordingly. The organic phase was continuous only when starting the agitator at high speed. Otherwise, the aqueous phase became continuous and remained so even when the agitator speed was increased.

3. With further increase of acid concentration, the densities and viscosities increased. However, $\Delta\rho$ did not necessarily increase, nor the proportional volume of the organic phase decrease, depending on the composition and the ternary diagram system. Nevertheless, the stable continuous phase was in most cases the aqueous phase and phase inversion was not possible even when starting the agitator at high speeds.

Another observation concerned with phase dispersion was that the settling time needed to achieve primary break was always shorter when the organic phase was continuous at low acid concentration. When this pattern prevailed with the acid concentration approaching the high concentration level, the settling time increased sharply in some cases, to more than 24 hours. With a continuous aqueous phase it increased slowly until the acid concentration was very high and even then it was less than 30 minutes.

Tri-n-butyl phosphate behaved differently. $\Delta\rho$ was almost negligible at low acid concentrations. The viscosity of the organic phase increased sharply while its volume percentage decreased with increasing acid concentrations.

9.2 OPTIMIZATION RESULTS

The results are reported in Appendix (X). It may be observed that:

1. The optimum values of phase ratios (R_E and K_p) were very near to their allowed minimum ($R_E m_E = 1$ and $m_i K_p = 1$) as represented by figure 9.2. This shows that minimization of the process flow rates is an important factor in minimizing the annual cost. The nature of the acid distribution curves would normally suggest a need for few contact stages but the limitations on the raffinate acid concentration made the throughput relatively high.

2. The total annual cost increased with decrease of acid concentration in the product (X_p), due to the added concentration cost and increased throughput of the whole plant. The cost also increased as expected when the level of impurity in the initial extract (C_{iYl}) and the solvent loss factor (ℓ) increased. The number of purification stages as well as the phase ratio (K_p) increases when using a solvent having low selectivity. The cost of lost solvent contributed appreciably to the total cost, and in some cases it was the highest individual cost. Efforts should, therefore, be focussed on minimizing the solvent losses.

3. The number of stages required was generally less than 2 for the extraction step, about 3 for the purification step and one for the washing step. With n-amyl alcohol, however, the number of purification stages increased to about 9 because of

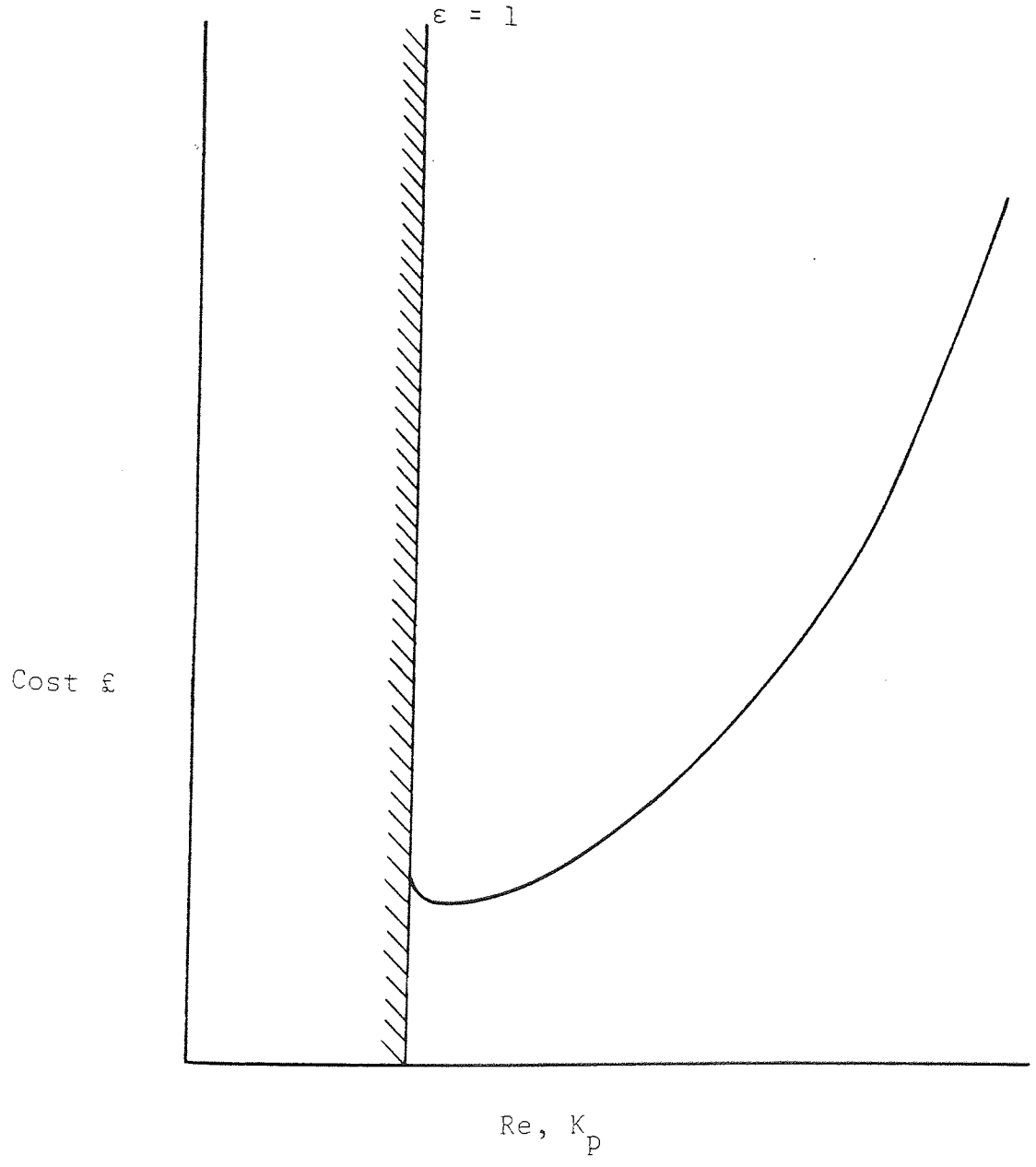


Fig.9.2 Effect of phase ratios in the extraction step (Re) and the purification step (K_p) on the manufacturing cost.

its low selectivity. With tri-n-butyl phosphate, on the other hand, the number of contact stages required for the extraction step increased to about 7 due to the low acid distribution coefficient.

4. The amount of raffinate produced is considerable. This may be a disadvantage if the raffinate treatment is highly expensive and if its use as a secondary product is not possible.

5. Comparison between the solvents showed that isopropyl ether was the optimum for the purification process, even with the same level of impurity in the initial extract (C_{iYl}). However, for the same feed, C_{IYl} will depend on the impurity distribution coefficient. Therefore, higher values of C_{IYl} are expected for n-amyl alcohol followed by methyl isobutyl ketone, di-isopropyl ether and tri-n-butyl phosphate, where the distribution coefficient of the impurities in the extraction step are approximately 0.3, 0.2, 0.1 and 0.08 respectively (figure 7.23) for the optimum attainable acid concentration.

6. The results obtained were based on a given set of data and parameters which were defined within known boundaries. However, the computation program could evaluate the optima for any other set of data and parameters. Test of any parameter can be easily performed which would be advantageous for process planning and control.

CHAPTER TEN

CONCLUSIONS

1. Solvent extraction can be successfully applied for the purification of wet-process phosphoric acid and could be competitive with the thermal process. However, this will depend on the extent of purification required and whether problems regarding the removal of anionic and organic impurities are overcome.

2. Iso-propyl ether is the most suitable solvent among those studied in this work. However, the possibility of peroxide formation may constitute a potential hazard. Therefore, the use of inhibitors and careful process design must be considered to eliminate the danger of explosions. Also, the three layer formation may cause operational difficulties. This should be overcome by precise flowrate control.

3. Powell's optimization method proved to be reliable and converged in all cases. The global optimum was checked by starting the search from a different starting point.

In addition, the following conclusions may be drawn on the physical and chemical properties.

4. An increase in the acid concentration in the system water-phosphoric acid - solvent would result in:

(i) increase of densities and viscosities of the phases;

(ii) decrease of the interfacial tension which results in smaller drops and longer settling time of the dispersed phase;

(iii) increase of the distribution coefficient of observed cationic impurities.

5. The presence of cationic impurities in the above system would:

(i) increase the heterogeneous area of the ternary phase equilibrium diagram;

(ii) reduce the distribution coefficient of the acid;

(iii) lengthen the settling time for mixtures containing low acid concentrations and vice versa.

6. With most systems the stable phase dispertion is W/O at low acid concentrations and O/W at high acid concentrations. Either phase can be made continuous at a medium acid concentration by controlling the starting agitator's speed.

7. Mono and divalent cations that can replace the strong phosphoric acid hydrogen react with the acid. Thus reducing its value as free acid. Also, this means that salts of these cations cannot be used as salting out agents when used alone.

8. The prediction of drop-size using Hinze's (32) equation did not agree with the experimental results. Unless the constant in the equation was corrected to account for the turbulance and physical properties of the system.

CHAPTER ELEVEN

RECOMMENDATIONS FOR FURTHER WORK

1. Study the nature of impurities present in wet-process phosphoric acid sludges, with especial emphasis on the anionic and organic impurities.

2. Study the extraction of simulated wet-process phosphoric acid solutions containing all important impurities at the same time. The effect of anionic and organic (if definable) impurities should be quantitatively analysed.

3. Study the extraction process at other temperatures ($5^{o}C$ and $40^{o}C$ for example) and apply the results in favour of the different solvent extraction steps.

4. Study the purification of wet process acid in conjunction with treatment by reagents to remove or enhance the separation of certain impurities prior to the extraction stage.

5. Search for a salting out agent which is appreciably soluble in low acid concentration solutions and non-reactive with the acid.

6. Study the acid purification process in a counter-current mixer settler unit making use of the information from this work.

7. The systems water - phosphoric acid - solvent provide ideal mixtures for the study of the effects of physical and dynamic properties on phase inversion.

8. The computer program developed in this work should be applicable to any other similar process. Minor modification of the objective function will enable the determination of optimum flowsheet and annual cost for any counter-current extraction process with reflux. The POWELL and CAMPEY sub-routines, however, will optimize any defined objective function in subrouteine YVALUE.

APPENDIX (I)

PHASE EQUILIBRIUM RESULTS WITH RESPECT TO PHOSPHORIC ACID AND IMPURITIES ACHIEVED IN THIS WORK

TABLE 1 : Composition along the binodal curve for water-phosphoric acid-n-amyl alcohol at 25°C

COMPOSITION wt %					
Water	Phosphoric acid	n-amyl alcohol	Water	Phosphoric acid	n-amyl alcohol
98.24	0.00	1.76	24.71	65.69	9.60
88.04	10.64	1.32	20.78	59.82	19.40
79.16	19.63	1.21	17.77	51.35	30.88
49.41	49.50	1.09	16.02	44.31	39.67
38.35	60.55	1.10	14.44	35.73	49.83
34.47	64.43	1.10	12.95	26.63	60.42
29.25	68.25	2.50	11.19	18.18	70.63
28.73	68.59	2.68	9.62	9.19	81.19
26.12	67.30	6.58	10.63	0.00	89.37
24.81	66.27	8.92			

TABLE 2 : Compositions of co-exisisting phases at equilibrium for water-phosphoric acid-n-amyl alochol at 25°C

Composition of upper layer wt%			Composition of lower layer wt%			Distribution Coefficient
Water	Phosphoric acid	n-amyl alcohol	Water	Phosphoric acid	n-amyl alcohol	
9.90	3.50	86.60	73.00	25.80	1.20	0.136
10.20	14.90	74.90	55.00	43.90	1.10	0.339
11.25	20.75	68.00	49.60	49.30	1.10	0.431
14.00	33.35	52.65	41.50	57.40	1.10	0.581
18.00	50.45	31.55	31.90	66.80	1.50	0.755

TABLE 3 : Composition along the binodal curve for water-phosphoric acid-n-amyl alcohol at 25°C, in the presence of a cationic impurity (0.5% Fe, Ca, Mg or 0.3% Al based on the aqueous phase)

COMPOSITION wt%					
Water	Phosphoric acid	n-amyl alcohol	Water	Phosphoric acid	n-amyl alcohol
98.24	0.00	1.76	19.70	63.20	17.10
87.62	11.24	1.14	17.00	56.40	26.60
79.10	19.92	0.98	14.30	48.30	37.40
70.55	28.50	0.95	12.00	39.00	49.00
58.42	40.63	0.95	10.60	30.20	59.20
46.90	52.15	0.95	9.30	22.30	68.40
35.80	63.23	0.97	8.00	14.00	78.00
28.05	70.05	1.90	7.90	7.60	84.50
26.20	70.90	2.90			
24.50	70.50	5.00			

N.B. The binodal curve fitted for all impurities within ± 0.5%

TABLE 4 : Composition of co-existing phases at equilibrium for water-phosphoric acid-n-amyl alcohol at 25°C in the presence of a cationic impurity (0.5% Fe, Ca, Mg or 0.3% Al based on the aqueous phase.)

Composition of upper layer wt%			Composition of lower layer wt%			Distribution coefficient
Water	Phosphoric acid	n-amyl alcohol	Water	Phosphoric acid	n-amyl alcohol	
9.20	3.40	87.40	77.34	25.70	0.96	0.132[a]
8.10	14.10	77.80	55.85	43.20	0.95	0.326[a]
9.00	20.15	70.85	49.75	49.30	0.95	0.409[a]
11.00	32.00	57.00	42.74	65.30	0.96	0.568[a]
14.30	48.00	37.70	32.50	66.50	1.00	0.722[b]
9.20	3.40	87.4	76.14	22.90	0.96	0.148[b]
8.20	14.30	77.5	59.35	40.65	0.95	0.352[b]
9.00	20.20	70.80	52.25	46.80	0.95	0.432[b]
11.00	32.00	57.0	44.84	54.20	0.96	0.590[b]
14.20	47.20	38.6	34.50	64.50	1.00	0.732[b]

(a) with 0.3% Al or 0.5% Fe in the initial aqueous acid

(b) with 0.3% Ca or 0.5% Mg in the initial aqueous acid

TABLE 5 : Compositions along the binodal curve for water-phosphoric acid-tri-n-butyl phosphate at 25°C

COMPOSITIONS wt %					
Water	Phosphoric acid	tri-n-butyl phosphate	Water	Phosphoric acid	tri-n-butyl phosphate
99.94	0.00	0.06	4.36	82.56	13.08
79.68	20.25	0.07	4.02	75.05	20.93
55.30	44.61	0.09	4.00	69.28	26.72
36.05	63.84	0.11	4.48	49.37	46.15
12.63	87.23	0.14	3.80	28.83	67.37
8.29	91.55	0.16	5.51	13.09	81.40
4.20	94.37	1.43	6.71	0.00	93.29
4.16	92.70	3.14			

TABLE 6 : Composition of co-existing phases at equilibrium for water-phosphoric acid tri-n-butyl phosphate at 25°C

Composition of upper phase wt%			Composition of lower phase wt%			Distribution Coefficient
Water	Phosphoric acid	tri-n-butyl phosphate	Water	Phosphoric acid	tri-n-butyl phosphate	
5.53	6.27	88.20	75.98	23.95	0.07	0.262
4.50	14.50	81.00	56.67	43.24	0.09	0.335
3.90	25.10	71.00	35.33	64.56	0.11	0.389
3.94	40.16	55.90	18.34	81.53	0.13	0.493
3.90	54.90	41.20	10.47	89.38	0.15	0.614

TABLE 7 : Composition along the binodal curve for the system water-phosphoric acid-tri-n-butyl phosphate at 25°C in the presence of a cationic impurity (0.5% Fe, Ca, Mg or 0.3% Al)

COMPOSITION wt %					
Water	Phosphoric acid	tri-n-butyl phosphate	Water	Phosphoric acid	tri-n-butyl phosphate
99.94	0.00	0.06	3.8	91.0	5.2
74.53	25.40	0.07	3.7	80.7	15.6
59.92	40.00	0.08	3.5	70.0	26.5
37.40	62.50	0.10	3.1	51.0	45.9
14.67	85.20	0.13	3.0	39.0	58.0
7.87	92.00	0.13	3.7	21.3	75.0
4.84	95.00	0.16	4.5	10.0	85.5
3.40	95.80	0.80	6.7	0.00	93.3

N.B. The binodal curve fitted all cases within $\pm$ 0.2%

TABLE 8 : Composition of co-existing phases at equilibrium for water-phosphoric acid-tri-n-butyl phosphate at 25°C in the presence of a cationic impurity (0.5% Fe, Ca, Mg or 0.3% Al of the initial raffinate)

Composition of upper layer wt%			Composition of lower layer wt%			Distribution Coefficient
Water	Phosphoric acid	tri-n-butyl phosphate	Water	Phosphoric acid	tri-n-butyl phosphate	
5.00	6.10	88.90	76.08	23.85	0.07	0.256[a]
4.10	14.30	81.60	56.72	43.20	0.08	0.331[a]
3.50	24.95	71.55	36.40	63.50	0.10	0.393[a]
3.00	40.00	57.00	19.38	80.50	0.12	0.497[a]
3.15	53.05	43.80	11.72	88.15	0.13	0.602[a]
5.00	6.10	88.90	77.03	22.90	0.07	0.266[b]
4.10	14.30	81.60	57.92	42.00	0.08	0.340[b]
3.50	24.90	71.60	37.70	62.20	0.10	0.400[b]
3.20	33.55	63.25	25.09	74.80	0.11	0.449[b]
3.00	40.60	56.40	20.59	79.30	0.12	0.512[b]
3.10	51.35	45.55	13.57	86.30	0.13	0.595[b]

(a) with mixtures containing 0.5% Fe or 0.3% Al in the initial aqueous acid.

(b) with mixtures containing 0.5% Ca or Mg in the initial aqueous acid.

TABLE 9 : Compositions along the binodal curve for H_2O - H_3PO_4 - di-isopropyl ether at 25%

COMPOSITION wt%					
Water	Phosphoric acid	di-iso propyl ether	Water	Phosphoric acid	di-iso propyl ether
98.80	0.00	1.20	19.54	69.61	10.85
88.75	10.15	1.10	15.35	61.65	23.00
78.90	20.05	1.05	13.17	56.68	30.15
68.62	30.08	1.30	9.44	48.93	41.63
58.50	40.00	1.50	6.29	41.37	52.34
48.75	50.00	1.25	4.08	34.80	61.12
38.82	60.08	1.10	3.16	30.63	66.21
31.02	67.25	1.73	0.32	0.00	99.68
26.23	70.54	3.23			

TABLE 10 : Compositions of the three layer region boundary for H_2O - H_3PO_4- di-isopropyl ether at 25°C

Composition wt% upper curve			Composition wt% lower curve		
Water	Phosphoric acid	di-iso propyl ether	Water	Phosphoric acid	di-iso propyl ether
30.15	68.00	1.85	30.15	68.00	1.85
21.60	56.20	22.20	23.80	54.20	22.00
13.50	45.35	41.15	18.00	42.00	40.00
5.38	30.62	64.00	13.90	32.50	53.60
3.70	23.20	73.10	11.95	28.20	59.85
0.40	5.50	94.10	0.40	5.50	94.10

TABLE 11 : Compositions of co-existing phases at equilibrium for H_2O - H_3PO_4 di-isopropyl ether at 25°C

Composition wt% upper layer			Composition wt% lower layer			Distribution Coefficient
Water	Phosphoric acid	di-iso propyl ether	Water	Phosphoric acid	di-iso propyl ether	
0.32	0.02	99.66	87.32	11.58	1.10	0.001
0.32	0.15	99.53	48.55	50.20	1.25	0.003
0.35	1.09	98.56	39.06	59.84	1.10	0.018
0.40	2.06	97.54	32.01	66.34	1.65	0.022
5.18	39.62	55.2	29.45	68.65	1.90	0.577
13.00	56.20	30.80	25.00	71.00	4.00	0.792

TABLE 12 : Composition of co-existing phases at equilibrium for H_2O - H_3PO_4–di-isopropyl ether at 25°C in the three phase region

Layer	COMPOSITION wt%		
	Water	Phosphoric acid	di-isopropyl ether
Upper	0.50	5.56	93.94
Middle	5.04	37.96	57.00
Lower	30.15	68.00	1.85

TABLE 13 : Composition along the binodal curve for the system water-phosphoric acid-di-isopropyl ether at 25°C in the presence of a cationic impurity (0.5% Fe, Ca, Mg or 0.3% Al of the aqueous phase).

COMPOSITION wt%					
Water	Phosphoric acid	di-iso-propyl ether	Water	Phosphoric acid	di-iso-propyl ether
98.80	0.00	1.20	22.07	72.60	5.33
87.60	11.40	1.00	17.66	69.40	12.94
68.60	30.20	1.20	13.85	63.90	22.25
43.33	45.40	1.27	12.85	62.70	24.50
40.03	59.00	0.97	10.83	56.60	32.57
30.40	68.50	1.10	5.55	43.20	51.25
23.15	73.20	3.65	4.95	40.10	54.95

N.B. The binodal curve fitted for all individual impurities within $\pm$ 0.3%

TABLE 14 : Co-existing phases composition for the system water-phosphoric acid-di-isopropyl ether at 25°C, in the presence of a cationic impurity (0.5% Fe, Ca, Mg or 0.3% Al of the aqueous phase).

Composition of upper layer wt%			Composition of lower layer wt%			Distribution Coefficient
Water	Phosphoric acid	di-iso-propyl ether	Water	Phosphoric acid	di-iso-propyl ether	
0.32	0.02	99.66	78.85	20.00	1.15	0.001
0.32	0.15	99.53	59.25	39.50	1.25	0.004
0.35	1.00	98.65	39.83	59.20	0.97	0.017
5.12	45.68	49.20	28.53	70.27	1.20	0.650[a]
9.23	53.62	37.15	25.77	72.43	1.80	0.740[a]
11.24	58.06	30.70	22.70	73.62	3.60	0.789[a]
5.09	43.71	51.20	29.25	69.65	1.10	0.628[b]
7.66	53.04	39.30	26.15	72.15	1.70	0.735[b]
10.18	56.22	33.60	24.90	73.00	2.10	0.770[b]
6.05	45.55	48.40	29.91	69.04	1.05	0.660[c]
8.62	52.48	38.90	27.13	70.97	1.90	0.739[c]
10.04	55.76	34.20	26.67	71.83	1.50	0.776[c]

(a) with mixtures containing 0.3% Al in the initial aqueous acid

(b) with mixtures containing 0.5% Fe in the initial aqueous acid

(c) with mixtures containing 0.5% Ca or Mg in the initial aqueous acid

TABLE 15 : Composition along the binodal curve for H_2O - H_3PO_4-methyl isobutyl ketone at 25°C

COMPOSITION wt%					
Water	Phosphoric acid	MIBK	Water	Phosphoric acid	MIBK
98.65	0.00	1.35	25.87	57.34	16.79
88.29	10.36	1.35	20.86	50.60	28.54
68.36	30.29	1.35	17.63	44.46	37.91
58.23	40.25	1.52	13.99	36.69	49.32
48.46	49.75	1.79	9.92	27.26	62.82
37.80	59.38	2.82	7.14	19.39	73.47
34.88	61.67	3.45	4.71	10.19	85.10
31.80	62.24	5.96	2.03	0.00	97.97

TABLE 16 : Compositions of co-existing phases at equilibrium for H_2O - H_3PO_4–methyl isobutyl ketone at 25°C

Composition of upper layer wt%			Composition of lower layer wt%			Distribution Coefficient
Water	Phosphoric acid	MIBK	Water	Phosphoric acid	MIBK	
2.10	0.02	97.88	92.39	6.26	1.35	0.003
2.10	0.05	97.85	81.19	17.46	1.35	0.003
2.20	0.72	97.08	51.30	47.00	1.70	0.015
2.40	1.85	95.75	46.48	51.72	1.80	0.036
2.80	3.70	93.50	44.24	53.86	1.90	0.069
6.94	17.76	75.30	38.32	58.93	2.75	0.301
16.18	42.02	41.80	33.05	62.85	4.10	0.669

TABLE 17 : Composition along the binodal curve for the system water-phosphoric acid-methyl isobutyl ketone at 25°C, in the presence of a cationic impurity (0.5% Fe, Ca, Mg or 0.3% Al of the aqueous phase)

COMPOSITION wt%					
Water	Phosphoric acid	MIBK	Water	Phosphoric acid	MIBK
98.65	0.00	1.35	28.82	63.70	7.48
68.20	30.50	1.30	24.00	58.80	17.20
45.70	52.60	1.70	17.00	49.50	33.50
40.65	57.40	1.95	11.28	38.10	50.62
34.15	62.80	3.05	4.96	20.10	74.94
32.10	63.80	4.10	3.90	11.30	84.80

N.B. The binodal curve fitted all individual impurities within ± 0.25%

TABLE 18 : Composition of coexisting phases at equilibrium for water-phosphoric acid methyl-isobutyl ketone at 25°C, in the presence of a cationic impurity (0.5% Fe, Ca, Mg or 0.3% Al of the aqueous phase)

Composition of upper layer wt%			Composition of lower layer wt%			Distribution Coefficient
Water	Phosphoric acid	MIBK	Water	Phosphoric acid	MIBK	
2.10	0.02	97.88	92.35	6.30	1.35	0.003
2.10	0.05	97.85	81.15	17.50	1.35	0.003
3.00	0.70	96.30	51.40	46.90	1.70	0.015
4.74	16.96	78.30	39.87	58.13	2.00	0.292[a]
11.45	38.75	49.80	34.24	62.76	3.00	0.617[a]
4.23	14.77	81.10	39.90	58.10	2.00	0.254[b]
11.39	38.11	50.50	34.56	62.54	2.90	0.609[b]
4.20	15.60	80.20	40.80	56.30	1.95	0.277[c]
11.11	37.40	51.50	37.40	59.80	2.80	0.625[c]

(a) with mixtures containing 0.3% Al in the initial aqueous acid

(b) with mixtures containing 0.5% Fe in the initial aqueous acid

(c) with mixtures containing 0.5% Ca or Mg in the initial aqueous acid

TABLE 19 : Concentration of H_3PO_4 and impurity in the coexisting phases at equilibrium at 25°C for water-impure phosphoric acid-n-amyl alcohol

Feed Impurity		Upper Phase (extract)		Lower Phase (raffinate)		Distribution Coefficient	
Name	p.p.m.	H_3PO_4 wt%	Impurity p.p.m.	H_3PO_4 wt%	Impurity p.p.m	H_3PO_4	Impurity
Fe	5000	3.40	9	25.70	5300	0.132	0.002
Fe	5260	14.17	90	43.20	6200	0.326	0.0145
Fe	5200	20.15	325	49.30	6200	0.409	0.0524
Fe	5270	32.00	700	56.30	6400	0.568	0.1094
Fe	5260	48.00	1900	66.50	6500	0.722	0.2923
*Fe	8870	52.3	3800	69.3	11200	0.755	0.3393
Al	3800	3.4	nil	25.70	4100	0.132	0.000
Al	4000	14.1	19	43.20	4800	0.326	0.004
Al	4100	20.15	100	49.30	4900	0.409	0.0204
Al	4200	32.00	340	56.30	5200	0.568	0.0654
Al	4300	48.00	1250	66.50	6250	0.722	0.200
*Al	6050	52.3	2620	69.3	7450	0.755	0.3516
Ca	5800	3.4	nil	22.90	6100	0.148	0.000
Ca	5850	14.3	200	40.65	7800	0.352	0.0256
Ca	5800	20.2	240	46.80	6900	0.432	0.0341
Ca	6000	32.00	440	54.20	7170	0.590	0.0614
Ca	5500	47.20	1630	64.50	6080	0.732	0.2681
*Ca	78	52.3	40	69.3	87	0.755	0.460
Mg	5200	14.3	16	40.65	6280	0.352	0.0025
Mg	5200	20.2	35	46.80	6400	0.432	0.0055
Mg	5500	32.0	182	54.20	6570	0.590	0.0277
Mg	5000	47.2	730	64.50	6200	0.732	0.1177
*Mg	2950	52.3	1000	69.30	4000	0.755	0.2500

* Wet-process phosphoric acid

TABLE 20 : Concentration of H_3PO_4 and impurity in the coexisting phases at equilibrium at 25°C for water-impure acid-n-tributyl phosphate

Feed Impurity		Upper Phase (extract)		Lower Phase (raffinate)		Distribution Coefficient	
Name	Concentration p.p.m.	H_3PO_4 wt%	Impurity p.p.m.	H_3PO_4 wt%	Impurity p.p.m.	H_3PO_4	Impurity
Fe	5240	25.0	124	63.5	5900	0.394	0.021
*Fe	8870	35.0	710	73.4	10550	0.477	0.0673
Fe	5200	40.0	330	80.5	5800	0.497	0.0566
Fe	5150	53.0	600	88.15	5500	0.601	0.1090
Al	2950	25.0	23	63.5	3200	0.394	0.0072
*Al	6050	35.0	238	73.4	7340	0.477	0.0320
Al	2700	40.0	77	80.5	2940	0.497	0.0262
Al	2470	53.0	174	88.15	2650	0.601	0.0657
Ca	3900	24.9	39	62.20	4340	0.400	0.0090
Ca	4100	33.5	85	74.80	4370	0.449	0.0195
*Ca	78	35.0	15	73.40	88	0.477	0.1705
Ca	3100	40.6	97	79.30	3530	0.512	0.0275
Mg	4800	24.9	6	60.0	5330	0.415	0.0011
*Mg	2950	35.0	61	73.4	3620	0.477	0.0169
Mg	5100	37.8	50	74.7	6130	0.506	0.0082
Mg	4700	51.3	750	84.3	5060	0.609	0.1482

*Wet-process phosphoric acid

TABLE 21 : Concentration of H_3PO_4 and impurities in the coexisting phases at equilibrium at 25°C for water- impure phosphoric acid - di-isopropyl ether

Feed Impurity		Upper Phase (extract)		Lower Phase (raffinate)		Distribution Coefficient	
Name	Concentration p.p.m.	H_3PO_4 wt%	Impurity p.p.m.	H_3PO_4 wt%	Impurity p.p.m.	H_3PO_4	Impurity
Fe	5000	0.15	nil	39.5	5100	0.004	0.000
Fe	5000	44	320	69.5	6700	0.633	0.048
*Fe	8870	52.8	816	70.7	12830	0.747	0.0636
Fe	3000	56.2	240	73.0	4280	0.770	0.0561
Al	1000	45.70	32	70.3	1650	0.650	0.0194
Al	950	53.6	54	72.4	1570	0.747	0.0344
*Al	6050	52.8	280	70.7	9000	0.747	0.0311
Al	950	56.2	53	73.0	1380	0.770	0.0384
Ca	6000	0.15	nil	39.5	6100	0.004	0.000
Ca	5200	1.0	nil	60.2	5500	0.017	0.000
*Ca	78	52.8	21	70.7	1004	0.747	0.210
Ca	2500	56.0	120	72.8	3600	0.770	0.0333
Mg	3200	45.55	55	69.04	3900	0.660	0.0141
*Mg	2950	52.8	85	70.3	4280	0.747	0.0199
Mg	1950	55.76	77	71.83	2800	0.776	0.0275

* Wet-process phosphoric acid

TABLE 22 : Concentration of H_3PO_4 and impurities in the coexisting phases at equilibrium at 25°C for water - impure phosphoric acid - methyl isobutyl ketone

Feed Impurity		Upper Phase (extract)		Lower Phase (raffinate)		Distribution Coefficient	
Name	Concentration p.p.m.	H_3PO_4 wt%	Impurity p.p.m.	H_3PO_4 wt%	Impurity p.p.m.	H_3PO_4	Impurity
Fe	5000	0.7	nil	46.90	5100	0.015	0.000
Fe	5200	34.2	575	60.80	6500	0.563	0.0885
Fe	5050	38.1	610	62.54	7000	0.609	0.0871
*Fe	8870	44.6	1370	64.70	10540	0.689	0.1300
Al	2700	16.96	115	58.13	2850	0.292	0.0040
Al	2550	38.75	210	62.76	3600	0.617	0.0583
*Al	6050	44.6	950	64.70	7430	0.689	0.1279
Ca	6300	15.60	20	56.30	6800	0.277	0.0029
Ca	6250	37.40	520	59.80	8100	0.625	0.0642
*Ca	78	44.6	23	64.70	85.8	0.689	0.268
Mg	4100	15.6	11	56.30	4400	0.277	0.0025
Mg	3900	37.4	160	59.80	5200	0.625	0.0308
*Mg	2950	44.6	316	64.30	3800	0.689	0.0832

* Wet-process phosphoric acid

TABLE 23. Concentration of H_3PO_4 and impurities in the co-existing phases at equilibrium at 25° for water - wet - process phosphoric acid - Solvent

SOLVENT		Feed concentration p.p.m.				Upper phase (extract) H_3PO_4	Upper phase (extract) p.p.m				Lower phase (raffinate) H_3PO_4	Lower phase (raffinate) p.p.m.				Distribution coefficient H_3PO_4	Fe	Al	Ca	Mg
		Fe	Al	Ca	Mg	wt.%	Fe	Al	Ca	Mg	wt.%	Fe	Al	Ca	Mg					
n-amyl alcohol	1	8870	6050	78	2950	52.3	3800	2620	40	1000	69.3	11200	7 50	87	4000	0.755	0.292	0.352	0.460	0.250
	2	3800	2620	40	1000	57.0	1600	900	24.6	390	69.2	2600	2000	53.6	840	0.824	0.615	0.450	0.460	0.463
tri-n-butyl phosphate	1	8870	6050	78	2950	35.0	710	238	15	61	73.4	10550	7340	88	3620	0.477	0.067	0.032	0.171	0.017
	2	710	238	15	61	32.9	43	9	9	1	74.4	580	200	40	60	0.442	0.074	0.045	0.225	0.017
di-iso propyl ether	1	8870	6050	78	2950	52.8	816	280	21	85	70.7	12830	9000	100	4280	0.747	0.064	0.031	0.210	0.02
	2	816	280	21	85	53.3	180	28.5	7.3	7	70.7	800	283	20.1	95	0.754	0.225	0.101	0.363	0.074
methyl isobutyl ketone	1	8870	6050	78	2950	44.6	1370	950	23	316	64.7	10540	7430	85.8	3800	0.689	0.130	0.128	0.268	0.083
	2	1370	950	23	316	50.7	580	318	8	100	62.9	1390	800	20	350	0.806	0.417	0.398	0.40	0.286

Note: (i) The first row (1) of each solvent represents an extraction stage for H_3PO_4 from feed - wet - process acid, while the second row (2) represents a purification stage for the extract produced in the extraction stage.

(ii) The phase ratio in the extraction stage is such as to give 1:1 water to solvent weight ratio. In the purification stage it is 1:1 by weight, extract to pure equilibrium raffinate.

APPENDIX (II)

PHASE EQUILIBRIUM DATA FOR THE SYSTEM WATER - PHOSPHORIC ACID - SOLVENT ACHIEVED BY OTHER WORKERS

TABLE 1. Compositions of Coexisting Phases at Equilibrium in the System Phosphoric Acid - Water - n - Amyl Alcohol at 25°C. (145)

Composition of upper layer (wt.%)			Composition of lower layer (wt.%)			Partition coefficient
phosphoric acid	water	n-amyl alcohol	phosphoric acid	water	n-amyl alcohol	
-	9.80	90.20	-	97.40	2.60	-
2.56	10.0	87.44	9.38	89.12	1.50	0.273
2.96	10.04	87.00	17.09	81.91	1.00	0.173
3.55	9.95	86.50	24.22	74.78	1.00	0.147
4.58	9.92	85.50	29.50	69.50	1.00	0.155
7.81	10.00	82.19	33.82	65.18	1.00	0.231
10.46	10.34	79.20	39.20	59.80	1.00	0.266
16.78	11.00	72.22	45.09	53.91	1.00	0.372
21.85	12.00	66.15	49.20	49.80	1.00	0.444
28.54	13.00	58.46	57.10	41.90	1.00	0.500
45.30	16.60	38.10	66.87	30.30	2.83	0.677

TABLE 2. Composition of Coexisting Phases at Equilibrium in the System Phospheric acid - water - cyclohexanol at 25°C. (146)

Tie line No.	Composition of upper layer (wt.%)			Composition of lower layer (wt.%)			Partition coefficient
	phospheric acid	water	cyclo-hexanol	phosphoric acid	water	cyclo-hexanol	
1	-	11.30	88.70	-	96.30	3.70	-
2	1.02	11.48	87.50	12.42	84.80	2.78	0.0821
3	2.14	11.66	86.20	17.64	80.03	2.33	0.1213
4	3.15	11.85	84.70	21.49	76.41	2.10	0.1605
5	4.52	11.88	83.60	23.78	74.10	2.12	0.1901
6	5.25	12.00	82.75	25.45	72.55	2.00	0.2063
7	5.39	12.01	82.60	26.62	71.38	2.00	0.2025
8	8.03	12.30	79.67	29.80	68.20	2.00	0.2695
9	8.71	12.49	78.80	31.36	66.64	2.00	0.2777
10	13.44	13.16	73.40	37.90	60.10	2.00	0.3546
11	17.63	14.00	68.37	41.62	56.38	2.00	0.4235
12	25.82	15.70	58.48	47.67	50.43	1.90	0.5416
13	29.34	16.66	54.00	51.74	46.46	1.80	0.5670
14	31.52	17.28	51.20	52.90	45.28	1.82	0.5958
15	39.06	19.90	41.04	57.06	41.06	1.88	0.6845
16	46.71	23.39	29.90	60.70	37.10	2.20	0.7695

TABLE 3. Compositions of Coexisting Phases at Equilibrium in the System Phosphoric Acid - Water - Dipropyl Ether at 25°C. (148)

Composition (wt.%)						
aqueous phase			dipropyl ether phase			Partition coefficient
phosphoric acid	water	dipropyl ether	phosphoric acid	water	dipropyl ether	
-	99.83	0.17	-	0.24	99.76	-
16.33	83.47	0.20	0.00	0.24	99.76	0.000
29.48	70.32	0.20	0.00	0.24	99.76	0.000
44.24	55.36	0.40	0.00	0.24	99.76	0.000
59.50	40.10	0.40	0.00	0.24	99.76	0.000
73.24	26.06	0.70	8.70	0.70	90.60	0.119

TABLE 4. Composition of Coexisting Phases at Equilibrium in the System Phosphoric Acid - Water - Ether at 25°C. (149)

Aqueous phase			Organic phase			Partition coefficient
phosphoric acid(wt.%)	ether (wt.%)	water (wt.%)	phosphoric acid(wt.%)	ether (wt.%)	phosphoric acid(wt.%)	
Phosphoric acid - water - di-isopropyl ether						
13.88	1.10	85.02	0	99.62	0.38	0
25.39	1.10	73.51	0	99.62	0.38	0
35.63	1.10	63.27	0	99.62	0.38	0
48.90	1.10	50.00	0.10	99.50	0.40	0.002
55.94	1.20	42.86	0.46	99.40	0.14	0.008
64.31	2.70	32.99	3.82	95.20	0.98	0.059
Phosphoric acid - water - dibutyl ether						
8.79	0.20	91.01	0	99.34	0.66	0
20.61	0.20	79.19	0	99.34	0.66	0
32.28	0.20	67.52	0	99.34	0.66	0
47.84	0.20	51.96	0	99.34	0.66	0
63.39	0.20	36.41	0	99.34	0.66	0
77.10	0.20	22.70	12.50	86.57	0.93	0.162
Phosphoric acid - water - di-isoamyl ether						
16.09	0.19	83.72	0.06	0.64	99.3	0.004
31.95	0.19	67.86	0.10	0.64	99.26	0.003
43.59	0.19	56.22	0.12	0.64	99.24	0.003
53.23	0.19	46.58	0.14	0.70	99.16	0.003
62.75	0.19	37.06	0.19	0.80	99.01	0.003
74.34	0.19	25.47	7.30	0.90	91.80	0.098
85.29	0.19	14.52	27.75	1.36	70.89	0.325

TABLE 5. Compositions of Coexisting Phases at Equilibrium in the System Phosphoric Acid - Water - Cyclohexanone at 25°C. (150)

Tie line No.	Aqueous phase (wt.%)			Cyclohexane phase (wt.%)			Partition Coefficient
	phosphoric acid	water	cyclohexa-none	phosphoric acid	water	cyclohexa-none	
1		91.37	8.63		76.47	23.53	-
2	7.38	84.64	7.98	0.17	5.32	94.51	0.0230
3	15.54	76.68	7.78	0.69	6.12	93.19	0.0444
4	23.48	67.91	8.61	3.43	9.00	87.57	0.1461
5	27.17	63.47	9.36	4.67	9.59	85.74	0.1719
6	30.17	58.38	11.45	9.15	12.89	77.96	0.3033
7	32.00	52.00	16.00	16.00	17.91	66.09	0.4923

TABLE 6. Compositions of Coexisting Phases at Equilibrium in the System Phosphoric Acid - Water - Methyl Ethyl Ketone at 25°C. (150)

Tie line No.	Aqueous phase (wt.%)			Methyl ethyl ketone phase (wt.%)			Partition co-efficient
	phosphoric acid	water	methyl ethyl ketone	phosphoric acid	water	methyl ethyl ketone	
1	-	76.47	23.53	-	11.53	88.47	-
2	3.00	74.09	22.91	0.22	11.78	88.00	0.0733
3	7.47	69.11	23.42	0.81	12.82	86.37	0.1084
4	12.79	61.40	25.81	2.40	14.67	82.93	0.1876
5	14.41	51.71	33.88	5.38	19.31	75.31	0.3734

TABLE 7. Compositions of Coexisting Phases at Equilibrium in the System Phosphoric Acid - Water - Methyl Hexyl Ketone at 25°C. (151)

Contents in aqueous phase (wt.%)			Contents in methyl hexyl ketone phase (wt.%)			
phos-phoric acid	water	methyl hexyl ketone	phos phoric acid	water	methyl hexyl ketone	Partition coeffi-cients
-	99.81	0.19	-	1.12	98.88	-
16.23	83.59	0.18	0.06	1.09	98.85	0.004
29.77	70.03	0.2	0.16	1.10	98.74	0.005
42.09	57.69	0.22	0.61	1.21	98.18	0.015
49.89	49.91	0.20	1.98	1.43	96.59	0.040
63.68	36.11	0.21	15.26	3.40	81.34	0.240
72.22	27.48	0.30	32.1	7.41	60.49	0.445

TABLE 8. Compositions of Coexisting Phases at Equilibrium in the System Phosphoric Acid - Water - Diisobutyl Ketone at 25°C. (151)

Contents in aqueous phase (wt.%)			Contents in diisobutyl ketone (wt.%)			
phosphoric acid	water	diisobutyl ketone	phosphoric acid	water	diisobutyl ketone	Partition coefficients
-	99.81	0.19	-	1.41	98.59	-
16.45	83.36	0.19	0	1.41	98.59	0
29.71	70.11	0.18	0	1.41	98.59	0
44.64	55.19	0.17	0	1.41	98.59	0
54.87	44.78	0.35	0.02	1.41	98.57	0
69.98	29.42	0.60	0.53	1.41	98.06	0.008
80.80	18.50	0.70	1.12	1.35	97.53	0.014

TABLE 9. Compositions of Coexisting Phases at Equilibrium in the System Phosphoric Acid - Water - n - Alkyl Acetates at 25°C.(152)

Aqueous phase (wt.%)			Organic phase (wt.%)			
phospho-ric acid	water	ester	phospho-ric acid	water	ester	Partition coefficient
		Phosphoric acid - water - ethyl acetate				
9.47	84.49	6.04	0.00	3.58	96.42	0.000
16.13	77.83	6.04	0.10	3.60	96.30	0.006
24.12	70.18	5.70	0.16	3.65	96.19	0.007
32.25	60.05	7.70	0.26	3.70	36.04	0.008
39.35	52.65	8.00	0.61	3.73	95.66	0.016
45.19	44.81	10.00	2.60	4.10	93.30	0.091
		Phosphoric acid - water - butyl acetate				
16.08	13.01	0.91	0.00	1.46	98.54	0.000
29.83	69.23	0.94	0.00	1.46	98.54	0.000
40.81	48.25	0.94	0.11	1.46	98.43	0.003
50.09	40.90	1.01	0.22	1.50	98.28	0.004
58.34	40.56	1.10	0.60	1.60	97.80	0.011
65.54	33.36	1.10	7.70	2.30	90.00	0.118
		Phosphoric acid - water - amyl acetate				
16.17	83.64	0.19	0.00	1.20	98.80	0.000
29.79	70.92	0.19	0.00	1.20	98.80	0.000
44.91	54.90	0.19	0.00	1.20	98.80	0.000
60.80	39.01	0.19	0.21	1.30	98.49	0.004
73.41	25.99	0.60	4.10	1.60	94.30	0.056

TABLE 10. Compositions of Coexisting Phases at Equilibrium in the System Phosphoric Acid - Water - Benzaldehyde at 25°C. (154)

Tie line No.	Composition of aqueous phase (wt.%)			Composition of benzaldehyde phase (wt.%)			Partition coefficient K_p
	phosphoric acid	water	benzalde-hyde	phosphoric acid	water	benzalde-hyde	
1	0.00	99.67	0.33	0.00	0.30	99.70	0
2	15.93	83.38	0.69	0.00	0.30	99.70	0
3	28.71	70.58	0.71	0.80	0.30	98.90	0.0278
4	44.00	55.18	0.82	4.98	1.21	93.81	0.1132
5	51.10	48.05	0.85	4.01	1.22	94.77	0.0980
6	57.30	41.81	0.89	5.11	1.25	93.64	0.0888
7	60.66	38.41	0.93	5.38	1.56	93.06	0.0887
8	69.16	29.83	1.01	12.92	3.09	83.99	0.1868

TABLE 11. Composition of Coexisting Phases at Equilibrium in the System Phosphoric Acid - Water - Salicylaldehyde at 25°C. (154)

Tie line No.	Aqueous phase (wt.%)			Salicylaldehyde phase (wt.%)			Partition coefficient K_p
	water	phosphoric acid	salicylal-dehyde	water	phosphoric acid	salicylal-dehyde	
1	99.42	0	0.58	0.98	0	99.02	0
2	83.48	15.82	0.70	0.98	0	99.02	0
3	80.90	28.50	0.60	0.98	0	99.02	0
4	58.89	40.50	0.61	0.98	0	99.02	0
5	49.25	51.35	0.40	0.98	0	99.02	0
6	39.80	59.60	0.60	0.97	0.1	99.02	0.0017
7	29.60	69.50	0.90	0.95	0.15	98.90	0.0022
8	23.81	74.74	1.45	1.10	0.20	98.70	0.0027
9	11.00	76.70	2.30	1.11	0.39	98.50	0.0051
10	17.28	78.00	4.72	1.22	0.93	97.85	0.0119

APPENDIX (III)

INTERFERANCE OF CALCIUM AND MAGNESIUM WITH PHOSPHORIC ACID

During the analysis by pH titration of phosphoric acid solutions containing calcium or magnesium phosphate impurities, it was noticed that the first and second end points were not equivalent, as was the case with pure and impure acid solutions containing ferric or aluminium phosphates. This was further investigated with acid solutions containing different concentrations of calcium and magnesium phosphates, and the results are given in Table 1 and figures 1 and 2. It is clear from the curves that as the concentration of these impurities increase, the first titration end point (strong acid hydrogen concentration) decreases and the second end point (first weak acid hydrogen ion concentration) increases. The proposed explanation of this phenomenon was described by the following chemical reation:

$$Ca_3(PO_4)_2 + 4H_3PO_4 \rightarrow 3Ca(H_2PO_4)_2 \qquad (1)$$

The four phosphoric acid molecules (each containing one strong, one weak and one very weak acid hydrogen ions) were replaced by three mono calcium biphosphate molecules (each containing two weak and two very weak acid hydrogen ions). This meant a 50% increase in the weak acid hydrogen concentration which is generally in agreement with the experimental

results obtained with calcium phosphate. However, the weak acid hydrogen ion concentration increase obtained with magnesium phosphate was lower, which suggested, that the following reactions are taking place:

$$Mg_3(PO_4)_2.6H_2O + 4H_3PO_4 \rightarrow 3Mg(H_2PO_4)_2 + 6H_2O \qquad (2)$$

$$Mg_3(PO_4)_2.6H_2O + 3H_3PO_4 \rightarrow 3Mg\ H_2PO_4 + 6H_2O \qquad (3)$$

Therefore, while the strong acid hydrogen ion has been replaced by magnesium in both reactions with a resulting 50% increase in the weak acid hydrogen from reaction No. 2, the latter is also replaced by magnesium in reaction No.3

In accordance with above, the concentration of free H_3PO_4 in impure acid solutions was always based on the strong hydrogen ion concentration. The above phenomenon was always noticed in wet-process phosphoric acid samples.

In general, di- as well as mono-valent cations are expected to interfere with the hydrogen ions of phosphoric acid. Further investigation may be needed if a completely satisfactory conclusion is required.

The solubility of calcium and magnesium phosphates increased sharply with increase in H_3PO_4 concentration of the aqueous solution to a maximum at a certain H_3PO_4 concentration, above which it decreases with further H_3PO_4 increase. The solubility of $Ca_3(PO_4)_2$ is shown in figure 3.

TABLE 1 : Titration of phosphoric acid samples in the presence of divalent cationic impurities

Sample No	Salt	Weight gm	Salt gm/100ml initial acid	0.1 N NaOH Titn.ml		H^+ Concentration	
				1st end point	2nd end point	1st end point	2nd end point
1	none	0.645	0.00	23.7	23.7	36.01	36.01
2	$Ca_3(PO_4)_2$	0.523	2.525	17.2	20.1	32.23	37.66
3	"	0.994	5.300	28.65	40.2	28.24	39.63
4	"	0.613	6.382	17.2	24.6	27.63	39.33
5	"	0.744	10.192	16.3	31.8	21.47	41.89
6	$Mg_3(PO_4)_2.6H_2O$	0.732	2.543	25.0	26.9	33.47	36.01
7	"	0.760	5.325	21.90	29.3	28.24	37.78
8	"	1.139	8.484	27.50	42.5	23.66	36.57
9	"	0.895	11.734	18.0	34.2	19.71	37.45

$$H^+ \text{ wt\%} = 0.98 \times \frac{\text{mls. of 0.1N NaOH}}{\text{gms. of sample}}$$

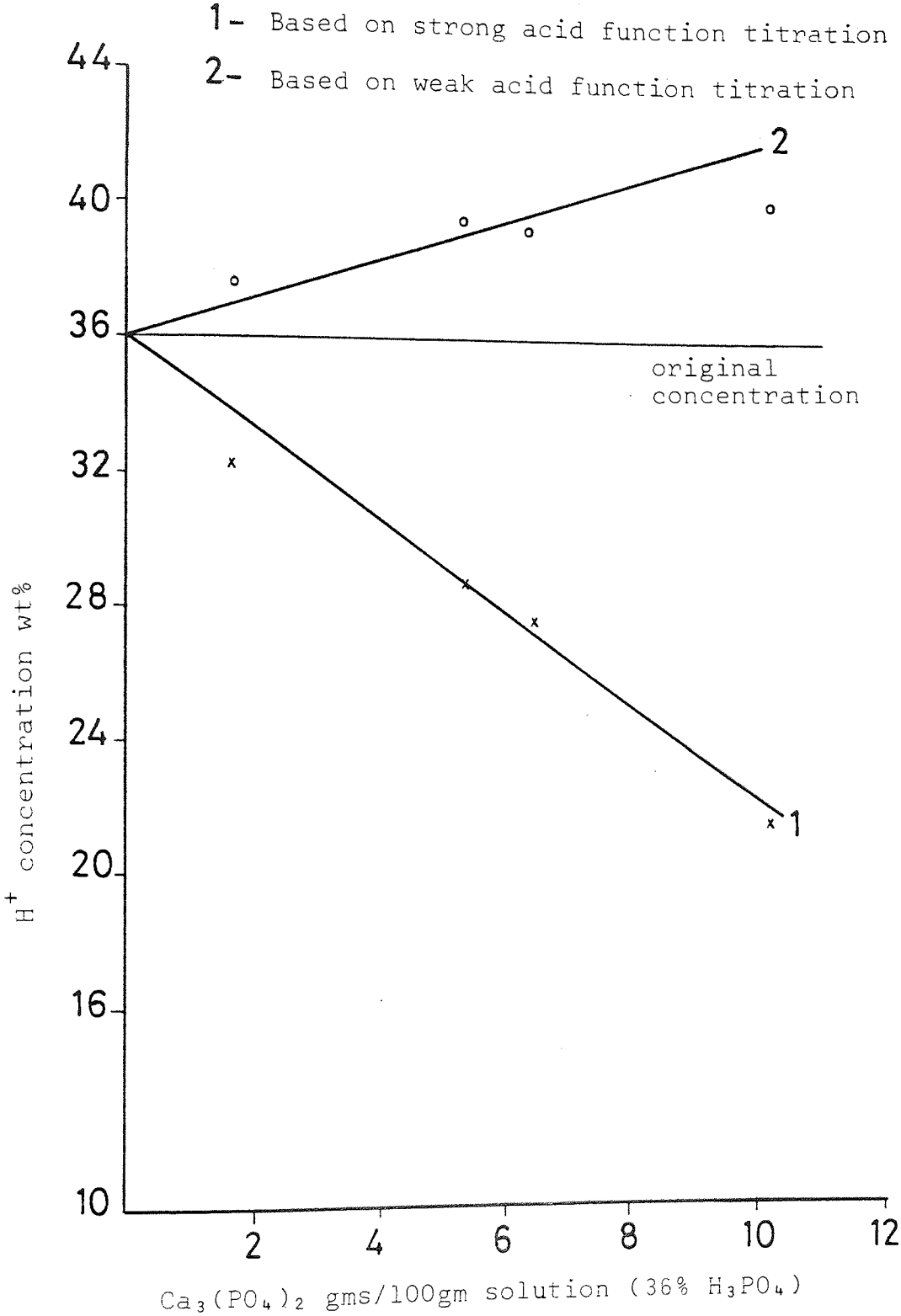


Fig.1 Effect of $Ca_3(PO_4)_2$ on the hydrogen ion concentration of phosphoric acid solution.

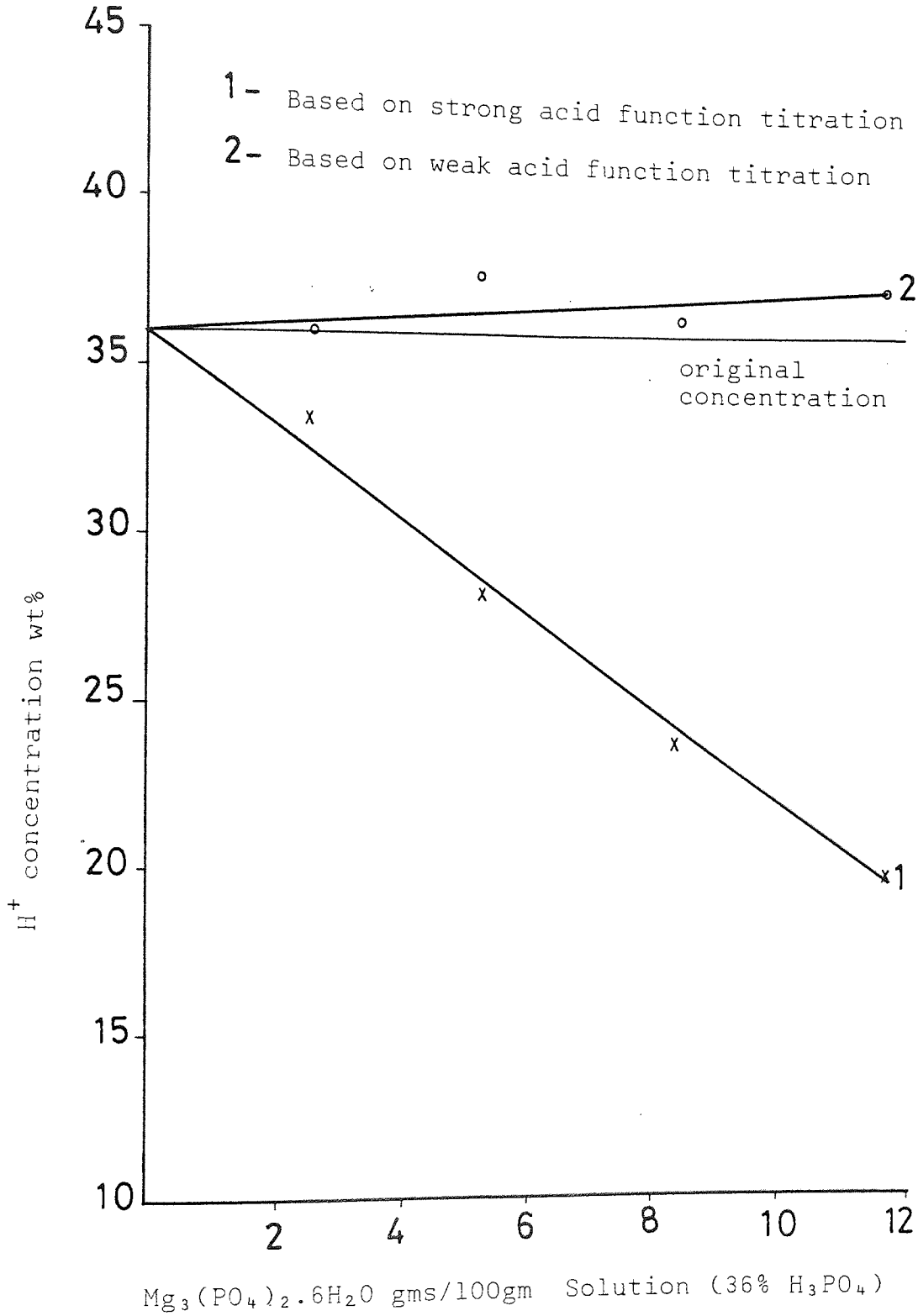


Fig.2 Effect of $Mg_3(PO_4)_2.6H_2O$ on the hydrogen ion concentration of a phosphoric acid solution

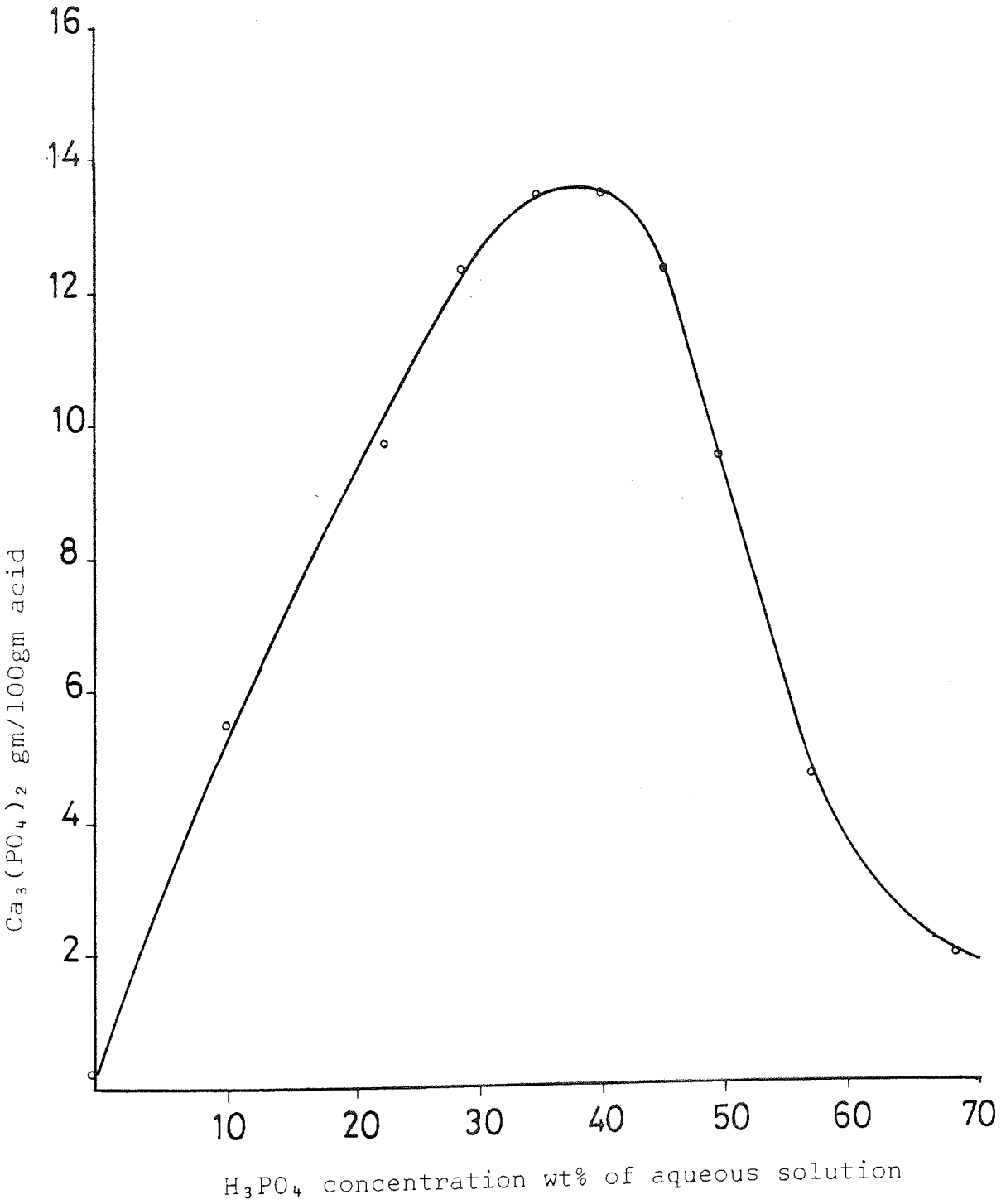


Fig. 3 Solubility of $Ca_3(PO_4)_2$ in aqueous phosphoric acid solutions at room temperature

APPENDIX (IV)

OPTIMIZATION OF THE PURIFICATION OF WET-PROCESS PHOSPHORIC ACID BY ANALYTICAL METHODS

The quantities that may be varied to produce the optimum design, corresponding to the minimum total manufacturing cost, are listed in Table 1 together with the terms in equation (5.1) that are influenced by each.

Since very little has been published on extractor design and its effect on extractor cost, it will not be considered as a variable. The concentration of impurities and H_3PO_4 in the final product will be fixed by the desired quality and therefore not subject to optimization. The concentration of solvent remaining in the finished product and raffinate cannot be optimized under the prevailing assumption of completely immiscible solvent with aqueous phase made in the flow-sheet calculations. However, after locating the optimum from the other controlled independent variables, the effect of variables number 7 and 8 and the subsequent recovery cost of the solvent can be calculated and optimized independently.

Accordingly, only X_n, Y_s, R_E and K_p will be varied to obtain the optimum. Phase ratio of water to solvent in the washing step is not an independent variable but a function of R_E and K_p as follows:

TABLE 1 : Quantities to be Optimized

	Quantity	Cost Item affected
1.	Design of extractor	I, III, IV
2.	Concentration of H_3PO_4 in the raffinate X_n (impure acid)	I, II , IV
3.	Concentration in the recycled solvent Y_s	I, IV
4.	Solvent to feed ratio in the extraction step R_E	I, IV, V
5.	Recycle to extract ratio in the purification step K_p	III, IV
6.	Concentration of impurities in the finished product C_{ixp}	III
7.	Concentration of solvent in the finished product	II, V
8.	Concentration of solvent in the finished raffinate	V, VI
9.	Concentration of H_3PO_4 in the final product X_p	IV, VI

An overall H_3PO_4 balance (figure 8.1)

$$F.X_F + W.0 = P.X_p + A.X_n \qquad (1)$$

$$(A-R).X_F = (W-R).X_p + A.X_n \qquad (2)$$

$$K_P = \frac{R(1+X_o)}{B(1+Y_1)} \qquad (3)$$

rearranging equation (2), dividing over B and substituting equation (3) in (2) gives:

$$\frac{1}{R_E}(X_F-X_n) = R_W.X_p - K_p\frac{(X_p-X_F)(1+Y_1)}{(1+X_o)}$$

or

$$R_W = \frac{(X_F-X_n)(1+X_o) + K_p.R_E(X_p-X_F)(1+Y_1)}{X_p-R_E(1+X_o)} \qquad (4)$$

(i) Effect of H_3PO_4 concentration in the raffinate X_n.

$$\frac{\partial C_t}{\partial X_n} = \frac{\partial I}{\partial X_n} + \frac{\partial II}{\partial X_n} + \frac{\partial IV}{\partial X_n} = 0 \qquad (5)$$

$$\frac{\partial I}{\partial X_n} = \frac{C_E}{E_{OE}} \frac{\partial n_E}{\partial X_n}$$

$$= \frac{C_E}{E_{OE}} \left\{ \frac{1 - \frac{1}{m_E R_E}}{\ell n m_E R_E} \right\} \left\{ \frac{-\left(X_F - \frac{Y_s - b}{m_E}\right)}{\left(X_F - \frac{Y_s - b}{m_E}\right)\left(1 - \frac{1}{m_E R_E}\right)} \right. \quad \cdots$$

$$\cdots \left. \frac{}{\left(X_n - \frac{Y_s - b}{m_E}\right) + \frac{1}{m_E R_E}} \left(X_n - \frac{Y_s - b}{m_E}\right)^2 \right\} \qquad (6)$$

$$\frac{\partial II}{\partial X_n} = A.L \qquad (7)$$

Assuming that $(X_p - X_F)$ is negligable (no enriching) equation (4) can be rewritten as

$$R_W = \frac{X_F - X_n}{X_p \cdot R_E} \qquad (8)$$

and

$$Y_o = Y_1 = \frac{X_F - X_n}{R_E} + Y_s \qquad (9)$$

$$\therefore \quad n_w = \frac{\log \left\{ \frac{X_F - X_n}{R_E Y_s} - \frac{X_p}{Y_s \cdot m_w} \right\}}{\log \left\{ m_w \frac{X_F - X_n}{X_p \cdot R_E} \right\}} \qquad (10)$$

$$\frac{\partial IV}{\partial X_n} = \frac{C_W}{E_{OW}\left\{\ell n\ m_W\left(\frac{X_F - X_n}{X_p \cdot R_E}\right)\right\}^2} \cdot \left\{\frac{-\ell n\ m_W \dfrac{X_F - X_n}{X_p \cdot R_E}}{R_E\left(\dfrac{X_F - X_n}{R_E} - \dfrac{X_p}{m_W}\right)} + \frac{\ell n\left\{\dfrac{X_F - X_n}{Y_s \cdot R_E} - \dfrac{X_p}{Y_s \cdot m_W}\right\}}{X_F - X_n}\right\} \qquad (11)$$

(ii) Effect of H_3PO_4 concentration in the recycled solvent Y_s.

$$\frac{\partial C_T}{\partial Y_s} = \frac{\partial I}{\partial Y_s} + \frac{\partial IV}{\partial Y_s} = 0 \qquad (12)$$

$$= \frac{C_E}{E_{OE}} \frac{\partial n_E}{\partial Y_s} + \frac{C_W}{E_{OW}} \frac{\partial n_W}{\partial Y_s} = 0$$

$$\frac{\partial I}{\partial Y_s} = \frac{C_E}{E_{OE}} \left\{\frac{1 - \frac{1}{m_E R_E}}{\ell n m_E R_E}\right\} \left\{\frac{(X_F - \frac{Y_s - b}{m_E}) - (X_n - \frac{Y_s - b}{m_E})}{m_E\left\{(X_F - \frac{Y_s - b}{m_E})\right.} \cdot\cdot\right.$$

$$\cdot\cdot \left.\frac{}{(1 - \frac{1}{m_E R_E}) / (X_n - \frac{Y_s - b}{m_E}) + \frac{1}{m_E R_E}\right\} (X_n - \frac{Y_s - b}{m_E})^2} \qquad (13)$$

$$\frac{\partial IV}{\partial Y_s} = \frac{C_W}{E_{OE} \ell n\ m_W R_W} \cdot \frac{-(m_W R_W - 1)}{(Y_s(m_W R_W - 1) + \frac{Y_s^2}{Y_c}} \qquad (14)$$

(iii) Effect of solvent to feed ratio in the extraction step R_E

$$\frac{\partial C_T}{\partial R_E} = \frac{\partial I}{\partial R_E} + \frac{\partial IV}{\partial R_E} + \frac{\partial V}{\partial R_E} = 0 \qquad (15)$$

$$\frac{\partial I}{\partial R_E} = \frac{1}{E_{OE}} \cdot \frac{\partial C_E \, n_E}{\partial R_E}$$

$$\frac{\partial IV}{\partial R_E} = \frac{1}{E_{OW}} \frac{\partial C_W \, n_W}{\partial R_E}$$

$$\frac{\partial V}{\partial R_E} = \ell . S.H \cdot \frac{\partial}{\partial R_E} \left(\frac{n_E}{E_{OE}} + \frac{n_W}{E_{OW}}\right) . B$$

(iv) Effect of recycle to extract ratio in the purification step K_p

$$\frac{\partial C_T}{\partial K_p} = \frac{\partial III}{\partial K_p} + \frac{\partial IV}{\partial K_p} = 0 \qquad (16)$$

$$\frac{\partial C_T}{\partial K_p} = \frac{1}{E_{op}} \frac{\partial C_p n_p}{\partial K_p} + \frac{1}{E_{OW}} \frac{\partial C_W n_W}{\partial K_p} = 0$$

In the general case, the number of stages, the cost per stage and the stage efficiency are influenced by R_E and K_p. Even if the efficiencies are considered to be constant, it is still very difficult to carry out the first partial differentiation of equations (15) and (16). It is recommended, therefore, that the optimum R_E and K_p be obtained by plotting a

contour describing C_T against R_E and K_p, calculating the cost with optimum values of X_n and Y_s. The minimum of the contour then locates $R_{E,opt.}$ and $K_{p,opt}$.

However, the solution of the simultaneous equations derived to calculate optimum X_n and Y_s at each given value of R_E and K_p can be difficult due to the complicated nature of the equations. Moreover, a direct optimization method may be needed to evaluate the optimum R_E and K_p values.

Therefore, it is not adviseable to carry out the optimization of this kind of process by analytical methods.

APPENDIX (V)

DETAILED CALCULATION OF THE ANNUAL COST PER STAGE C_E

$$C_E = C_{VE}\left(\frac{p}{y} + b^*\right) + (P_A + P_P)W.H$$

C_{VE}. the purchase cost of a complete mixer-settler was based on published costs (166) of a particular unit for a similar duty, as follows:

Mixer volume m^3	Settler volume m^3	Material of Construction	Year	Cost*
5.8 m^3	20	P.V.C. + Fiber glass reinforced polyester	1970	£ 7000

*Cost is for a complete mixer-settler unit including electric motor (explosion proof) and variable speed drive. The settler is of a compact type. Two pumps were assumed per stage. The power requirement (P_P) was calculated as follows (184):

$$P_P = (\Delta H)(G)(S)/3960 \qquad (1)$$

where ΔH = differential head (ft)

G = fluid flow rate (gal/min)

S = specific gravity

Equation (1) can be rewritten

$$P_P = \Delta H \times Q/1350$$

where Q is fluid flow rate (tons/day) and ΔH is differential height (m).

The residence time in the mixer was assumed to be 10 mins. (taken from figure 7.47). A 5.8 m^3 mixer may handle a maximum:

$$Q = 5.8 \times \rho_{av} \times \frac{60}{10} \times 24 = 1100 \text{ ton/day}$$

where ρ_{av} is assumed to be 1.3 (figure 7.49).

Assuming 3 metres differential height,

$$P_P = \frac{3 \times 1100}{1350} = 2.4 \text{ horse power.}$$

Assuming centrifugal pumps are used with an efficiency of 60%.

$$HP = \frac{2.4}{0.6} = 4 \text{ horse power pump is required for a 5.8 cu.m.mixer.}$$

Approximate cost of a 4hp pump in 1970 (184) = £400.

Plant cost index (185) in 1976 = 2.4

∴ Purchase cost of a complete mixer-settler unit + two pumps in 1976 = (7000 + 800) x 2.4 = £19000.

The purchase cost at other mixer capacities (q) is calculated by the 2/3 rule as follows:

$$C_{VE} = 19000\left(\frac{q}{5.8}\right)^{0.65}$$

The remaining terms in equation (1) are defined as follows:

$p = 1 + 1.6 = 2.6$

$y = 3$ years

$b^* = 0.1$ (10% of purchase cost)

$P_A = 1\text{hp/m}^3$ of fluid in the mixer

$$P_P = \frac{3 \times Q}{1350} = \frac{Q}{450} \text{ hp}$$

$1\text{hp} = 0.746\text{KW}$

Cost of 1KWH = £0.015

APPENDIX (VI)

Comparison between drop-size distribution results obtained from experimental work and those calculated by equation (9.7)

System : Water-phosphoric acid - Solvent, Mixtures at 1:1 water to solvent ratio

Solvent	H_3PO_4 wt%	Cont. Phase	ρ_c gm/cm³	σ dyne/cm	μ poise	N R.P.S.	$d_{3.2}$ mm Exp.	$d_{3.2}$ mm Calc.	% dev	Exp. k_1	Re	We
MIBK	2	Solvent	0.82	10.0	0.005	11.67	0.059	0.060	+ 1.7	0.713	17220	301
"	2	"	"	"	"	14.17	0.052	0.048	- 7.7	0.785	20910	444
"	2	"	"	"	"	20.00	0.040	0.032	-20.0	0.906	29520	886
"	6	"	"	9.2	0.006	10.83	0.050	0.062	+24.0	0.585	13325	282
"	6	"	"	"	"	13.33	0.045	0.048	+ 6.7	0.780	16400	428
"	6	"	"	"	"	16.67	0.041	0.037	- 9.8	0.803	20500	668
"	18	"	0.83	5.8	0.007	9.17	0.046	0.057	+24.0	0.585	9780	325
"	18	"	"	"	"	10.83	0.042	0.047	+11.9	0.648	11560	453
"	18	"	"	"	"	12.50	0.038	0.040	+ 5.3	0.689	13340	604
"	6	Water	1.03	9.2	0.014	6.67	0.062	0.090	+56.5	0.463	4410	134
"	6	"	"	"	"	8.33	0.050	0.075	+50.0	0.483	5520	210
IPE	11.9	Solvent	0.73	18.8	0.004	15.00	0.062	0.069	+ 9.6	0.657	25270	236
"	"	"	"	"	"	18.33	0.056	0.055	- 1.8	0.738	30880	352
"	"	"	"	"	"	21.67	0.051	0.045	-11.8	0.822	36500	492
"	25	"	"	17.3	"	12.50	0.053	0.082	+54.7	0.469	21200	179
"	"	"	"	"	"	15.00	0.048	0.066	+37.5	0.527	25440	258
"	"	"	"	"	"	18.33	0.042	0.052	+23.8	0.586	31100	386
"	43	"	0.74	10.1	0.0045	10.00	0.040	0.077	+92.5	0.377	14800	198
"	"	"	"	"	"	11.67	0.037	0.064	+73.0	0.419	17270	269

continued/

APPENDIX (VI) continued

Solvent	H_3PO_4 wt%	Cont. Phase	ρ gm/cm^3	σ dyne/cm	μ poise	R.P.S.	d_{32} mm Exp.	d_{32} mm Calc.	d_{32} mm % dev	Exp. k_1	Re	We
Alcohol	30	Water	1.25	3.3	0.026	6.67	0.035	0.047	+34.3	0.540	2880	455
"	"	"	"	"	0.026	8.33	0.030	0.036	+20.0	0.604	3600	710
"	45	"	1.35	1.6	0.042	5.83	0.039	0.034	-12.8	0.832	1690	775
"	"	"	"	"	0.042	6.67	0.032	0.029	- 9.4	0.800	1930	1013
T.B.P.	15	Solvent	1.02	7.5	0.11	5.83	0.073	0.102	+40.0	0.519	490	125
"	"	"	"	"	"	7.50	0.051	0.075	+47.0	0.493	625	207
"	"	"	"	"	"	10.00	0.039	0.053	+34.2	0.540	835	367
"	"	Water	1.15	"	0.021	5.00	0.063	0.114	+81.0	0.400	2460	104
"	"	"	"	"	"	6.67	0.040	0.081	+102.0	0.358	3290	184
"	"	"	"	"	"	8.33	0.035	0.062	+77.1	0.409	4110	288
"	30	"	1.26	6.7	0.04	5.83	0.063	0.084	+32.3	0.548	1650	173
"	"	"	"	"	"	8.33	0.035	0.055	+57.1	0.461	2360	353
"	50	"	1.43	5.4	0.112	5.00	0.055	0.082	+49.1	0.486	1420	179
"	"	"	"	"	"	6.67	0.040	0.058	+45.0	0.500	1890	318

APPENDIX (VII)

TYPICAL DROP-SIZE ANALYSIS COUNT

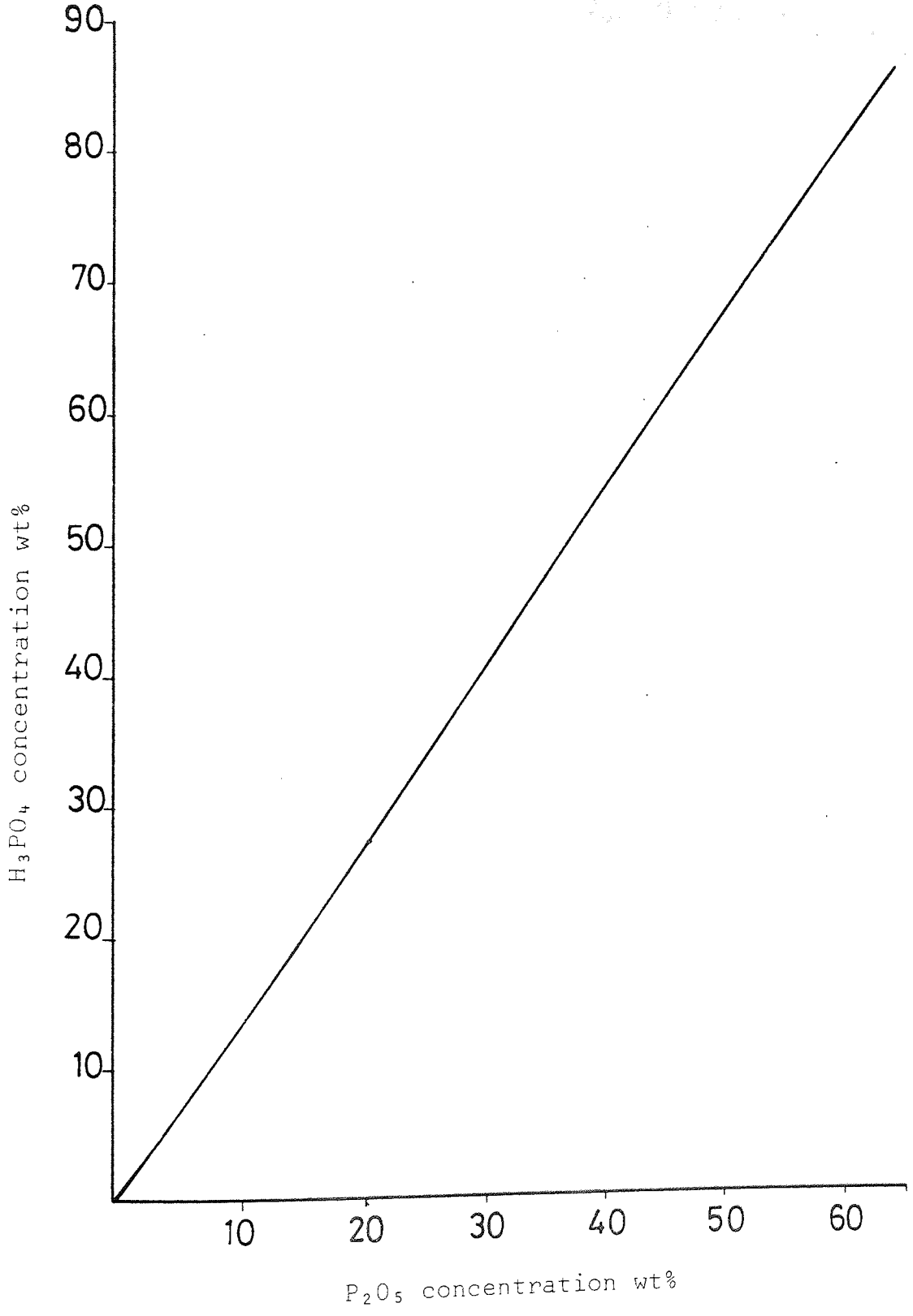
System : Water-phosphoric acid - di-isopropyl ether mixture at 1:1 by weight water to solvent, 11.19% H_3PO_4 of total batch, 850 RPM. Continuous phase : solvent phase. Magnification factor 4.0 x 3*

diameter d(mm)	n
4.80	0
5.35	4
5.90	19
7.01	42
7.56	75
8.11	52
8.66	37
9.22	30
9.77	16
10.32	4
10.87	0

$$d_{32} = \frac{\Sigma n.(\frac{d}{12})^3}{\Sigma n(\frac{d}{12})^2} = 0.651 \text{ mm.}$$

* By adjustment of the drop-size analysis equipment

APPENDIX (VIII)



H_3PO_4 vs. P_2O_5 concentrations in phoshporic acid solutions.

APPENDIX (IX)

OPERATING CONDITIONS FOR THE CHROMOTOGRAPHIC ANALYSIS OF SAMPLES CONTAINING METHYL ISO-BUTYL KETONE, WATER AND PHOSPHORIC ACID TO CHECK THE STABILITY OF THE SOLVENT

Equipment : Pye Series 104, Katherometer
Isothermal chromotograph, Model 34

Column : Stainless Steel

Column Packing Material : Porapak P.,

Oven Temperature : 200°C

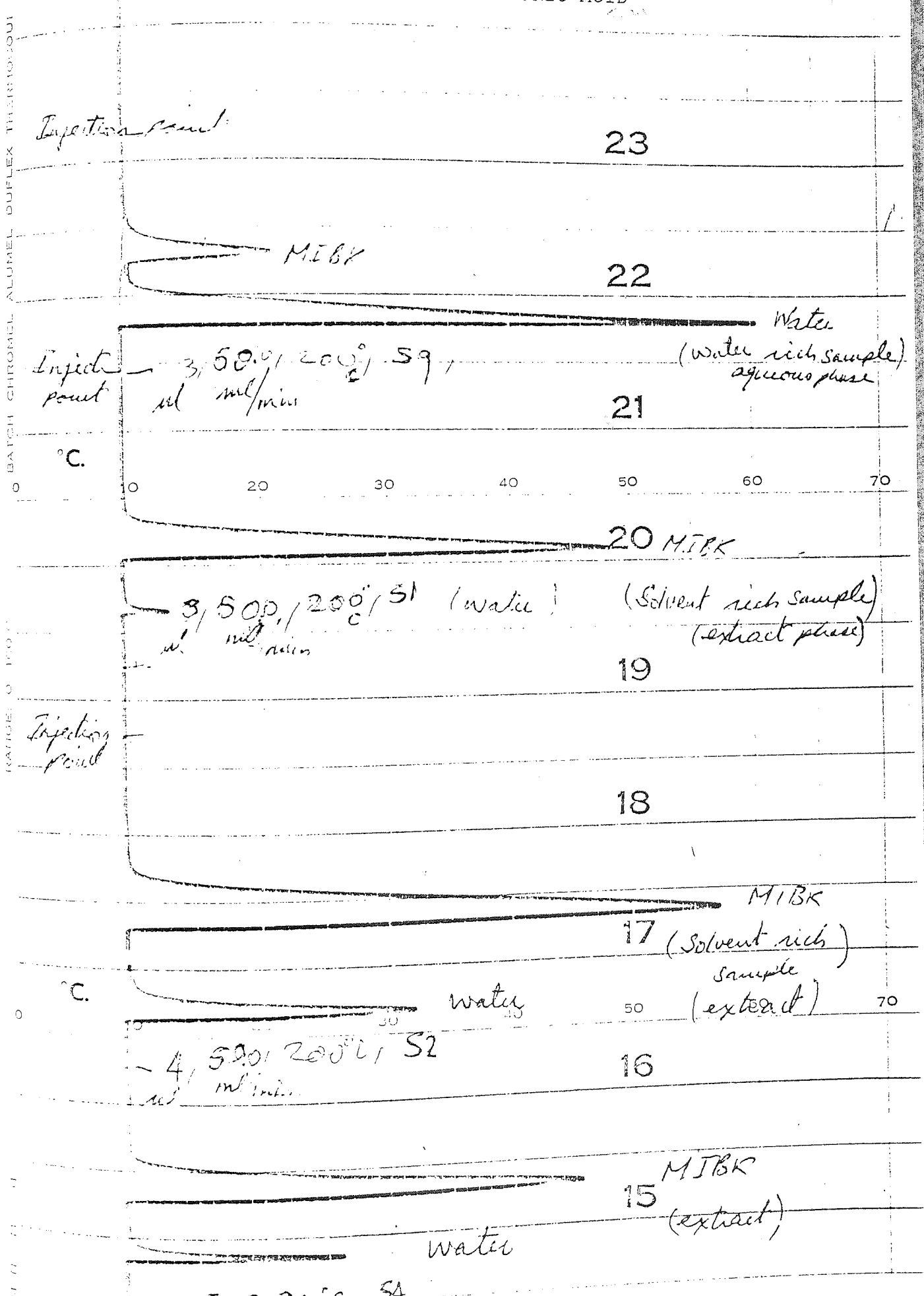
Injection Temperature : 100°C

Injection Sample Size : 1-5 µℓ

Carrier gas : Helium at 50 ml/min.

Chart speed : 30 inches/hr.

CHROMOTOGRAPHIC ANALYSIS FOR SAMPLES
CONTAINING METHYL ISO BUTYL KETONE,
WATER AND PHOSPHORIC ACID



APPENDIX (X)

OPTIMIZATION COMPUTATION
PROGRAM LIST OUT AND RESULTS

```
      MASTER YACU
      DIMENSION Z(10),U(40),COS(9,20),T(50,20),WAL(40,5)
      COMMON MIKE
C      NO. OF INDEPENDENT VARIABLES
      N=3
C      NO. OF DATA,PARAMETERS AND INDEPENDENT VARIABLES
      NIK=35
C      IF IP=-1 ONLY FINAL OUTPUT IS PRINTED, DETAILS WHEN IP=>1
      IP=-1
C      IF M2=-1,MINIMIZATION,IF M2=1,MAXIMIZATION
      M2=-1
C      NO. OF SOLVETS TESTED
      NOS=4
      LEE=0
      WRITE(2,208)
208   FORMAT(1H1,/////,10X,' PURIFICATION OF WET-PROCESS PHOSPHORIC',
     1' ACID BY SOLVENT EXTRACTION',//,10X,' WATER-PHOSPHORIC ACID-',
     1' SOLVENT',//,10X,' BASIC DATA,PARAMETERS AND INDEPENDENT',
     1' VARIABLES',//
     2,10X,' BASIS OF DESIGN AND COST EVALUATION; 100 TONS P2O5/DAY'//)
      WRITE(2,28)
28    FORMAT(51X,'IPE',9X,'ALCOHOL',5X,'MIBK',8X,'TBP')
C      INPUT DATA
      DO 24 JZ=1,NOS
      READ(1,349)(WAL(I,JZ),I=1,NIK)
24    CONTINUE
C      PRINT DATA
      WRITE(2,5 )((WAL(I,JZ),JZ=1,4),I=1,20)
      WRITE(2,53)((WAL(I,JZ),JZ=1,4) ,I=21,35)
5     FORMAT(10X,' IMP.CONCN.IN INITIAL EXTRACT(CIY1)%',4F12.5,/,
     110X,' IMP.CONCN.IN FINAL PRODUCT(CIXP)%',2X,4F12.5,/,
     210X,' IMP DIST.COEFF.(PURN.STEP)(MI)',5X,4F12.5,/,
     310X,' IMP.CONCN.IN FINAL EXTRACT(CIYC)%',2X,4F12.5,/,
     410X,' H3PO4 DIST.COEFF.(SLOPE ME)',8X,4F12.5,/,
     510X,' H3PO4 CONCN.,TONS/TON FEED,(XF)',4X,4F12.5,/,
     610X,' H3PO4 CONCN.,TONS/TON PRODUCT,(XP)',1X,4F12.5,/,
     710X,' H3PO4 DIST.LINE INTERCEPT(b*)',6X,4F12.5,/,
     810X,' PRODUCT FLOWRATE TONS/DAY(P)',7X,4F12.5,/,
     910X,' FEED DENSITY,TONS/C.M',14X,4F12.5,/,
     110X,' SOLVENT DENSITY,TONS/C.M',11X,4F12.5,/,
     210X,' RES.TIME IN MIXER,DAYS',13X,4F12.5,/,
     310X,' COST OF UNINSTALLED STANDARD STAGE#',4F12.5,/,
     410X,' CAPACITY OF STANDARD STAGE,C.M,',4X,4F12.5,/,
     510X,' FACTOR TO CALC.INSTALLED STAGE COST',4F12.5,/,
     610X,' PAY OUT TIME,YEARS,',10X,4F12.5,/,
     710X,' MAINT.ALLOWANCE FACTOR,10% CAPITAL',1X,4F12.5,/,
     810X,' POWER CONS.IN MIXER,HP/C.M',9X,4F12.5,/,
     910X,' PUMP OVERHEAD HEIGHT,M',13X,4F12.5,/,
     110X,' ELECTRICITY COST,#/KWH',13X,4F12.5)
53    FORMAT(10X,' WORKING DAYS PER YEAR,DAYS',9X,4F12.5,/,
     510X,' OVERALL STAGE EFFICIENCY',11X,4F12.5,/,
     410X,' RAFF.TREAT.COST,#/TON',14X,4F12.5,/,
     510X,' DENS.OF FINAL EXTRACT,TONS/C.M.',4X,4F12.5,/,
     610X,' H3PO4 DIST.COEFF.(WASH.STEP,MW)',4X,4F12.5,/,
     710X,' DENS. OF WATER,TONS/C.M.',11X,4F12.5,/,
     810X,' SOLVENT LOSS FACTOR,%,(L)',10X,4F12.5,/,
     910X,' COST OF SOLVENT,#/TON',14X,4F12.5,/,
     110X,' PRODUCT CONCN.COST,#/TON',11X,4F12.5,/,
     210X,' LOW ...ORG. CONCN. IN SOLVENT,TONS/TON',4F12.5,/,
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```
     410X,' TEST FACTOR OF YS',18X,4F12.5,/,
     510X,' PHASE RATIO IN PURN.STEP(KP)',7X,4F12.5,/,
     610X,' PHASE RATIO IN EXTN.STAGE(RE)',6X,4F12.5,/,
     710X,' H3PO4 CONCN.IN RAFF.(XN)TONS/TON',3X,4F12.5)
      WRITE(2,54)
54    FORMAT(//,10X,' THE ANNUAL LABOUR COST IS CONSTANT =#24000')
      DO 165 JZ=1,NOS
      DO 345 I=1,NIK
165   U(I)=WAL(I,JZ)
349   FORMAT(35F0.0)
482   FORMAT(6F10.4)
      DO 444 I=1,N
444   Z(I)=WAL(I+32,JZ)
447   FORMAT(3F0.0)
      IF(IP.GE.1)WRITE(2,18)
18    FORMAT(6X,'KP',8X,'RE',8X,'XN',8X,'XF',7X,'XP',8X,'P')
      IF(IP.GE.1)WRITE(2,482)(Z(I),I=1,N),U(6),U(7),U(9)
      NOMB=1
      DK=U(7)
      DOP=U(9)
      MR=0
61    U(7)=DK
      U(9)=DOP
163   MR=MR+1
       SENDING FOR POWELL TO GENERATE OPTIMIZATION PROCEDURE
      CALL POWELL(Z,MR,U,IP,N,M2,COS,T)
      T(39,MR)=U(31)
      DO 72 I=40,42
72    T(I,MR)=Z(I-39)
      T(43,MR)=U(7)
      T(44,MR)=U(1)
      T(45,MR)=U(27)
      IF(IP.GE.1)WRITE(2,75) U(31),(Z(I),I=1,N)
      IF(IP.GE.1)WRITE(2,131)(T(I,MR),I=1,6)
131   FORMAT(/' N1=',F7.4,2X,'N2=',F7.4,2X,'N3=',F7.4,2X,'Q1=',F7.4,
     12X,'Q2=',F7.4,2X,'Q3=',F7.4)
      IF(IP.GE.1)WRITE(2,132)(T(I,MR),I=7,12)
132   FORMAT(/' PA1=',F7.3,1X,'PA2=',F7.3,1X,'PA3=',F7.3,1X,'PP1='
     1,F7.3,1X,'PP2=',F7.3,1X,'PP3=',F7.3)
      IF(IP.GE.1)WRITE(2,133)(T(I,MR),I=13,18)
133   FORMAT(/' C1=',F8.2,2X,'C2=',F8.2,2X,'C3=',F8.2,2X,
     1'CS1=',F9.2,2X,'CS2=',F9.2,2X,'CS3=',F9.2)
      IF(IP.GE.1)WRITE(2,134)(T(I,MR),I=19,23)
      IF(IP.GE.1)WRITE(2,135)(T(I,MR),I=24,26),U(9),U(7),U(6)
134   FORMAT(/' Y1=',F8.5,2X,'X0=',F8.5,2X,'YC=',F8.5,
     12X,'B=',F8.3,2X,'R=',F8.3)
135   FORMAT(/' A=',F8.3,2X,'E=',F8.5,2X,'W=',F8.5,2X,'P=',F8.3,2X,
     1'XP=',F8.3,2X,'XF=',F8.3)
      IF(IP.GE.1)WRITE(2,516)
516   FORMAT(/' EXTN.COST',2X,'RAFF.LOSS',2X,'PURN.COST',2X,'WASH.COST'
     1,2X,'SOLV.LOSS',2X,'CONC.COST',2X,'TOTAL COST')
      IF(IP.GE.1)WRITE(2,84)(COS(I,MR),I=1,7)
75    FORMAT(' U(31)=',F5.4,2X,'KP=',F9.7,2X,'KE=',F9.7,2X,'XN=',F9.7)
       TESTING DIFFERENT VALUES OF YS
      U(31)=U(31)-U(32)
      IF(U(31).GE.U(30))GO TO 161
      U(31)=U(31)+U(32)
      IF(NOMB.GT.1)GO TO 96
```

```
C       TESTING DIFFERENT VALUES OF XP
        PROD=U(7)
        U(7)=U(7)-0.5
        IF(U(7).LT.0.5)GO TO 95
        U(9)=U(9)*PROD/U(7)
 95     IF(U(7).GE.0.5)GO TO 163
        NOMB=NOMB+1
 98     U(7)=DK
        U(9)=DOP
C       TESTING DIFFERENT VALUES OF LOSS FACTOR (L)
        U(27)=U(27)+0.0001
        IF(U(27).LE.0.0005)GO TO 163
        U(27)=0.0005
C       TESTING DIFFERENT VALUES OF EXTRACT IMPURITIES LEVEL (CIY1)
        U(1)=U(1)+1.0
        IF(U(1).LE.4.0)GO TO 163
 84     FORMAT(//7(F10.2,1X)//)
        LEE=LEE+1
        GO TO(571,572,573,574),LEE
571     WRITE(2,671)
        GO TO 103
572     WRITE(2,672)
        GO TO 103
573     WRITE(2,673)
        GO TO 103
C       PRINTING THE CLASSIFIED OUTPUT
574     WRITE(2,674)
671     FORMAT(1H1,///////,10X ,'THE SOLVENT IS DI-ISOPROPYL ETHER(IPE)'
     1//)
672     FORMAT(1H1,///////,10X ,'THE SOLVENT IS N-AMYL ALCOHOL'//)
673     FORMAT(1H1,///////,10X ,'THE SOLVENT IS METHYL ISO BUTYL KETONE',
     1' (MIBK)'//)
674     FORMAT(1H1,///////,10X,' THE SOLVENT IS TRI-N-BUTYL PHOSPHATE',_
     1' (TBP)'//)
103     WRITE(2,104)
104     FORMAT(//,10X,' THE INDEPENDENT VARIABLES AND PARAMETERS ARE'//)
        WRITE(2,190)
190     FORMAT(//,10X,' CASE NO.',5X,'YS',8X,'KP',8X,'RE',8X,'XN'
     1,8X,'XP',8X,'CIY1',2X,'LOSS/STAG*B'//)
106     FORMAT(1H1,///////,10X,' THE NO. AND CAPACITIES OF STAGES ARE'//)
        DO 30 JH=1,MR
        WRITE(2,32)JH,(T(I,JH),I=39,45)
30      CONTINUE
32      FORMAT(10X,I5,5X,7F10.5,/)
        WRITE(2,106)
        WRITE(2,191)
191     FORMAT(//,10X,' CASE NO.',3X,'N1(EXTN)',2X,'N2(PURN)',2X,
     1'N3(WASH)',2X,'Q1(EXTN)',2X,'Q2(PURN)',2X,'Q3(WASH)'/)
        DO 34 JH=1,MR
        WRITE(2,36)JH,(T(I,JH),I=1,6)
34      CONTINUE
36      FORMAT(10X,I5,5X,6F10.5,/)
        WRITE(2,108)
108     FORMAT(1H1,///////,10X,' THE FLOW-SHEET FLOWRATES AND',
     1' CONCENTRATIONS'//)
        WRITE(2,192)
192     FORMAT(//,10X,' CASE NO.',6X,'Y1',8X,'X0',8X,'YC',8X,'B',
     19X,'R',9X,'A',9X,'F',9X,'W',9X,'P'/)
        DO 38 JH=1,MR
        WRITE(2,39)JH,(T(I,JH),I=19,27)
38      CONTINUE
```

```
 39   FORMAT(10X,I5,5X,9F10.4,/)
      WRITE(2,110)
110   FORMAT(1H1,///////,10X,' THE STEPS AND FINAL COST,#'//)
      WRITE(2,195)
195   FORMAT(//,10X,' CASE NO.',4X,'EXTN.COST',3X,'RAFF.LOSS',1X,
     1' PURN.COST'
     1,3X,'WASH.COST',3X,'SOLV.LOSS',3X,'CONCN.COST',2X,'TOTAL COST'//)
      DO 193JH=1,MR
      WRITE(2,194)JH,(COS(I,JH),I=1,7)
193   CONTINUE
194   FORMAT(10X,I5,5X,7F12.3,/)
165   CONTINUE
      END
      SUBROUTINE POWELL(Z,MR,U,IP,N,MZ,COS,T)
C
C  NON LINEAR OPTIMIZATION USING POWEL'S METHOD AND DAVIES SWANN AND
C          CAMPEY'S ALGORITHIM FOR THE LINEAR SEARCHES
      DIMENSION X(9,9),V(9,9),COM(9,60),YR(50),XMIN(9,9),XOW(9,9),
     1FAU(10,2),Z(10),U(40),COS(9,20),T(50,20)
C      MIKE IS THE NO. OF FUNCTION EVALUATION
      COMMON MIKE
      NA=N+1
      IO=0
C      AQ IS ACCURACY TOLLERANCE BETWEEN TWO OPTIMUM POINTS
      AQ=0.001
      JIO=1
 82   MIKE=0
C      GENERATING ORTHOGONAL DIRECTION
      DO 159 I=1,N
      DO 154 J=1,N
      IF(I.EQ.J)GO TO 451
      V(I,J)=0.0
      GO TO 154
451   V(I,J)=1.0
154   CONTINUE
159   CONTINUE
      DO 20 I=1,N
 20   X(I,1)=Z(I)
      FO=1.0
      AQUA=5.0
 333  LD=0
 900  L=1
 545  IF(LD.GT.0)GO TO 7
      IF(AQUA.LE.5.0E-04)GO TO 5
      AQUA=AQUA/10.0
      FO=FO/10.0
      GO TO 5
  7   AQUA=5.0E-06
  5   DO 185 I=1,N
 185  COM(I,L)=X(I,1)
C      IF(L.EQ.1)GOTO 45
       COMPARISON OF OPTIMUM POINTS
      DO 580 I=1,N
      IF(ABS(COM(I,L)-COM(I,L-1)).GE.AQ) GO TO 45
 580  CONTINUE
      GO TO 600
 45   IF(IP.GE.1)WRITE(2,55)
 55   FORMAT(//15X,'YS',10X,'KP',10X,'RE',10X,'XN',12X,'COST',//)
  65  FORMAT(20X,3(F10.7,5X),F12.5)
```

```
      L=L+1
      DO 200 J=1,N
      J1=J+1
      IF(J.GT.1) GO TO 50
C      EVALUATION THE FUNCTION AT STARTING POINT
      CALL YVALUE(X,MR,U,YA,COS,J,T)
      YR(J)=YA
      IF (IP.GE.1) WRITE(2,65)(X(I,J),I=1,N),YR(J)
C      SEND FOR CAMPEY FOR LINEAR SEARCH
   50 CALL CAMPEY(X,MR,N,J,AQUA,V,XMIN,YA,FO,M2,U,COS,T)
      DO 90 I=1,N
   90 X(I,J1)=XMIN(I,J)
      YR(J1)=YA
      IF (IP.GE.1) WRITE(2,65)(X(I,J+1),I=1,N),YR(J+1)
  200 CONTINUE
      IF(IP.GE.1)WRITE(2,699) MIKE
      DO 210 I=1,N
  210 Z(I)=X(I,N+1)
      YF=YA
C     FINDING THE DIRECTION WHICH GAVE THE BEST CHANGE
      DIF=-M2*10000.0
      DO 220 J=1,N
      IF(M2*DIF.GE.M2*(YR(J1)-YR(J))) GO TO 220
      DIF=YR(J+1)-YR(J)
      KM=J
  220 CONTINUE
      IF (IP.GE.1) WRITE(2,218)KM
  218 FORMAT(//11X,
     1 11H VECTOR NO.,I2,30H GAVE THE BEST VARIATION IN Y )
C     DEFINING THE NEW DIRECTION(XN-XO)
      VNEW=0.0
      DO 240 I=1,N
  242 V(I,NA)=X(I,NA)-X(I,1)
  240 VNEW=VNEW+V(I,NA)**2
      VNEW=SQRT(ABS(VNEW))
      IF(VNEW.NE.0.0)GO TO 241
      DO 249 I=1,N
      Z(I)=X(I,N+1)
  249 CONTINUE
      GO TO 710
  241 IF (IP.GE.1) WRITE(2,1615)VNEW
 1615 FORMAT(//11X,' ABSOLUTE VALUE OF THE NEW VECTOR=',F12.7/)
       IF (IP.GE.2) WRITE(2,6132)(V(I,NA),I=1,N)
 6132 FORMAT(/3 (F10.7,3X))
      DO 350 I=1,N
  350 XOW(I,NA)=X(I,NA)+V(I,NA)
      J=NA
C     CALCN. THE OBJECTIVE FUNCTION AT X(2N) (F2)
      CALL YVALUE(XOW,MR,U,YJ,COS,J,T)
      HAM=(YR(1)-2*YR(NA)+YJ)*(YR(1)-YR(NA)-(-DIF))**2
      BEE=0.5*(-DIF)*(YR(1)-YJ)**2
C     TESTING THE NEW DIRECTION
      IF(M2*YJ.GT.M2*YR(1).OR.M2*HAM.GT.M2*BEE) GO TO 518
      IF(M2*YR(NA).GE.M2*YJ) GO TO 2455
      IF (IP.GE.1) WRITE(2,517)
  517 FORMAT(//11X,24H X(2N) IS A BETTER POINT/)
      DO 400 I=1,N
  400 X(I,1)=XOW(I,NA)
      GO TO545
```

```
2435 DO 380 I=1,N
 380 X(I,1)=X(I,NA)
     IF (IP.GE.1) WRITE(2,257)
 257 FORMAT(/11X,24H SO FAR X(N) IS THE BEST/)
     GO TO 545
C    INSERTING THE NEW SUCCESSFUL DIRECTION
 318 DO 243 I=1,N
 243 V(I,NA)=V(I,NA)/VNEW
     IF (IP.GE.2) WRITE(2,6132)(V(I,NA),I=1,N)
     DO 322 J=KM,N
     DO 316 I=1,N
 316 V(I,J)=V(I,J+1)
 322 CONTINUE
      IF (IP.GE.1) WRITE(2,329)
     IF (IP.LT.2) GO TO 330
     IF(IP.GE.1)WRITE(2,777)
 777 FORMAT(/,' THE NEW SET OF DIRECTIONS'/)
     IF(IP.GE.1)WRITE(2,6132)((V(I,J),J=1,N),I=1,N)
     IF(IP.GE.1)WRITE(2,2026)
2026 FORMAT(///)
 329 FORMAT(//33H THE BEST DIRECTION IS CONVERGENT/)
 330 J= N
     CALL CAMPEY(XMIN,MR,N,J,AQUA,V,XOW,YA,FO,M2,U,COS,T)
     DO 4002I=1,N
4002 X(I,1)=XOW(I,J)
     GO TO 545
 600 LD=LD+1
 620 DO 630 I=1,N
     FAO(I,LD)=COM(I,L)
 630 X(I,1)=FAO(I,LD)+10*AQUA*V(I,1)
     IF(LD.GT.1) GO TO 3402
     IF (IP.GE.1) WRITE(2,153)
C    TESTING THE OPTIMUM BY STARTING SEARCH FROM ANOTHER POINT
 153 FORMAT(/11X,43H THE OPTIMUM POINT IS INCREASED BY 10*AQUA/)
     GO TO 900
3402 J=1
     VNO=0
     DO 640 I=1,N
     V(I,J)=FAO(I,LD)-FAO(I,LD-1)
     X(I,J)=FAO(I,LD-1)
     VNO=VNO+V(I,J)**2
 640 CONTINUE
     VNO=SQRT(ABS(VNO))
     DO 647 I=1,N
 647 V(I,J)=V(I,J)/VNO
     CALL CAMPEY(X,MR,N,J,AQUA,V,XMIN,YF,FO,M2,U,COS,T)
     DO 680 I=1,N
     IF(ABS(FAO(I,LD-1)-XMIN(I,J)).GT.AQ.AND.ABS(FAO(I,LD)-XMIN(I,J)).G
    1T.AQ)GO TO 333
 680 CONTINUE
     IF(IP.GE.1)WRITE(2,699) MIKE
     IF(IP.GE.1)WRITE(2,990)
 699 FORMAT(//11X,I8,' FUNCTION EVALUATIONS HAVE BEEN PERFORMED'/)
 990 FORMAT(10X,' THE OPTIMUM IS AT THE POINT'/)
     IF (IP.LT.1) GO TO 690
     IF(IP.GE.1)WRITE(2, 65)(XMIN(I,J),I=1,N),YF
 690 CONTINUE
```

```
985 FORMAT(6(F12.7,2X))
    JIO=JIO+1
    DO 700 I=1,N
700 Z(I)=XMIN(I,J)
710 RETURN
    END
    SUBROUTINE YVALUE(X,MR,U,YA,COS,J,T)
C    CALCULATION FLO-SHEET DETAILS  AND CORRESPONDING COSTS
    DIMENSION X(9,9),U(40),COS(9,20),T(50,20),D(100)
    COMMON MIKE
C   MODIFICATION OF THE IMPURITIES DISTRIBUTION COEFF.
    DC=U(3)*U(7)/(U(7)+1.0)
 95 T(28,MR)=U(3)*X(1,J)
    IF(T(28,MR).GT.1.0)GO TO 37
C   THE CONSTRAINT(M,R) IS PREACHED
    T(28,MR)=1.0001
    X(1,J)=T(28,MR)/U(3)
    T(2,MR)=1000.0
    GO TO 21
 37 T(29,MR)=(((U(1)-U(2)/U(3))/(U(4)
   1-U(2)/U(3)))*(1.0-1.0/T(28,MR)))+1.0/T(28,MR)
    T(2,MR)=ALOG(T(29,MR))/ALOG(T(28,MR))
 21 T(30,MR)=U(5)*X(2,J)
    T(31,MR)=(U(31)-U(8))/U(5)
    IF(T(30,MR).GT.1.0)GO TO 27
    T(30,MR)=1.0001
    X(2,J)=T(30,MR)/U(5)
    T(1,MR)=1000.0
    IF(X(3,J).GT.T(31,MR))GO TO 23
    X(3,J)=T(31,MR)+0.00001
    GO TO 23
 27 IF(X(3,J).GT.T(31,MR))GO TO 23
    X(3,J)=T(31,MR)+0.00001
    T(1,MR)=1000.0
    GO TO 23
 19 T(32,MR)=((U(6)-T(31,MR))/(X(3,J)-T(31,MR)))*
   1(1.0-1.0/T(30,MR))+1.0/T(30,MR)
    T(1,MR)=ALOG(T(32,MR))/ALOG(T(30,MR))
 23 T(33,MR)=X(1,J)*U(5)
    IF(U(6).EQ.U(7))GO TO 45
    L=1
    D(L)=U(7)
 97 T(19,MR)=(X(1,J)*(D(L)-U(6))+((1.0/X(2,J))*(U(6)-X(3,J))
   1+U(31))*(U(7)+1.0))/((U(7)+1.0)-X(1,J)*(D(L)-U(6)))
    L=L+1
    T(34,MR)=T(33,MR)*(T(19,MR)+1.0)/(U(7)+1.0)
    D(L)=U(7)-(U(7)-((T(19,MR)-U(8))/U(5)))*(
   1(T(34,MR)**(T(2,MR)+1.0))-T(34,MR))/((T(34,MR)
   2**(T(2,MR)+1.0))-1.0)
    IF(ABS(D(L)-D(L-1)).GT.0.0001)GO TO 97
    T(20,MR)=D(L)
    GO TO 105
 45 T(20,MR)=U(7)
    T(19,MR)=(1.0/X(2,J))*(U(6)-X(3,J))+U(31)
105 T(21,MR)=T(19,MR)-X(1,J)*(T(20,MR)-U(7))*(T(19,
   1MR)+1.0)/(U(7)+1.0)
    IF((T(21,MR)-U(31))/U(7).GT.X(1,J)*(T(19,MR)+1.0)/(U(7
   1)+1.0))GO TO 29
```

```
      X(1,J)=((T(21,MR)-U(31))/U(7))/((T(19,MR)+1.0)/(U(7)
     1+1.0))-0.05
      T(28,MR)=U(3)*X(1,J)
      IF(T(28,MR).LT.1.0)GO TO 11
      GO TO 37
   11 IF(IP.GE.1)WRITE(2,13)
   13 FORMAT(' THAT IS SILLY,ENOUGH!')
      GO TO 95
   29 T(22,MR)=U(9)/(((T(21,MR)-U(31))/U(7))-X(1,J)*(T(
     119,MR)+1.0)/(U(7)+1.0))
      T(23,MR)=X(1,J)*T(22,MR)*(T(19,MR)+1.0)/(U(7)+1.0)
      T(24,MR)=T(22,MR)/X(2,J)
      T(25,MR)=T(24,MR)-T(23,MR)
      T(26,MR)=T(23,MR)+U(9)
      T(27,MR)=U(9)
      IF(T(30,MR).EQ.1.0001.OR.X(3,J).EQ.(T(31,MR)+0.00001))
     1GO TO 96
      T(38,MR)=(T(25,MR)*U(6)*T(25,MR)*T(20,MR))/
     1T(24,MR)
      T(32,MR)=((T(38,MR)-T(31,MR))/(X(3,J)-T(31,MR)))*
     1(1.0-1.0/T(30,MR))+1.0/T(30,MR)
      T(1,MR)=ALOG(T(32,MR))/ALOG(T(30,MR))
      GO TO 86
   96 T(1,MR)=1000.0
   86 T(4,MR)=(T(25,MR)*(U(6)+1.0)/U(10)+T(23,MR)*
     1(T(20,MR)+1.0)/U(10)+T(22,MR)*(U(31)+1.0)/
     2U(11))*U(12)
      T(13,MR)=U(13)*((T(4,MR)/U(14))**0.65)
      T(7,MR)=T(4,MR)*U(18)
      T(10,MR)=(T(25,MR)*(U(6)+1.0)+T(23,MR)*(T(20,MR)
     1+1.0)+T(22,MR)*(U(31)+1.0))*U(19)/1500.0
      T(16,MR)=T(13,MR)*(U(15)/U(16)+U(17))+(T(7,MR)+
     1T(10,MR))*U(20)*U(21)
C     ITEM 1 EXTRATION STAGE
      COS(1,MR)=T(1,MR)*T(16,MR)/U(22)
C     ITEM 2 RAFFINATE LOSS
      COS(2,MR)=T(24,MR)*X(3,J)*U(25)
      T(5,MR)=(T(22,MR)*(T(19,MR)+1.0)/U(24)+T(23,MR)
     1*(U(7)+1.0)/U(10))*U(12)
      T(14,MR)=U(13)*((T(5,MR)/U(14))**0.65)
      T(8,MR)=T(5,MR)*U(18)
      T(11,MR)=(T(23,MR)*(T(20,MR)+1.0)+T(22,MR)*
     1(T(19,MR)+1.0))*U(19)/1500.0
      T(17,MR)=T(14,MR)*(U(15)/U(16)+U(17))+
     1(T(8,MR)+T(11,MR))*U(20)*U(21)
C     ITEM 3 PURIFICATION STAGE
      COS(3,MR)=T(2,MR)*T(17,MR)/U(22)
      T(35,MR)=T(26,MR)/T(22,MR)
      T(36,MR)=T(35,MR)*U(25)
      T(37,MR)=(T(19,MR)/U(31))*(1.0-1.0/T(36,MR))+1.0/T(30,
     1MR)
      IF(T(36,MR).LE.1.0.OR.T(37,MR).LE.1.0)GO TO 92
      T(3,MR)=ALOG(T(37,MR))/ALOG(T(30,MR))
      GO TO 94
   92 PR=U(7)
      IF(U(7).GE.1.0)GO TO 81
      U(7)=U(7)-0.1
      GO TO 89
   81 U(7)=U(7)-0.5
   89 U(9)=PR*U(9)/U(7)
      U(3)=DC/(U(7)/(U(7)+1.0))
```

```
 94   T(6,MR)=U(12)*(T(22,MR)*(T(19,MR)+1,0)/U(24)+T(26,
     1MR)/U(26))
      T(15,MR)=U(13)*((T(6,MR)/U(14))**0,65)
      T(9,MR)=T(6,MR)*U(18)
      T(12,MR)=(T(26,MR)+T(22,MR)*(T(19,MR)+1,0))*U(19)
     1/1500,0
      T(18,MR)=T(15,MR)*(U(15)/U(16)+U(17))+(T(9,MR)
     1+T(12,MR))*U(20)*U(21)
C     ITEM 4 WASHING STAGE
      COS(4,MR)=T(3,MR)*T(18,MR)/U(22)
C     ITEM 5 SOLVENT LOSSES COST
      COS(5,MR)=((T(1,MR)+T(2,MR)+T(3,MR))/U(22))*
     1T(22,MR)*U(27)*U(28)
     2*U(21)
C      ITEM 6 CONCENTRATION COST
       COS(6,MR)=U(9)*U(7)*(U(6)-U(7))*U(29)*U(21)
C     TOTAL COST
      COS(7,MR)=COS(1,MR)+COS(2,MR)+COS(3,MR)+
     1COS(4,MR)+COS(5,MR)+COS(6,MR)+24000,0
      MIKE=MIKE+1
      YA=COS(7,MR)
      RETURN
      END
      SUBROUTINE CAMPEY(X,MR,N,J,Q,V,XMIN,YZ,FO,M2,U,COS,T)
      DIMENSION X(9,9),B(9,100),V(9,9),Y(100),XMIN(9,9),U(40),
     1COS(9,20),T(50,20)
      DATA KMAX/100/
      REAL M
      J1=J+1
      DO 40 I=1,N
 40   XMIN(I,J)=X(I,J)
C     DEFINING THE INITIAL STEP LENGTH
      S=5,0
      S=S*FO
 100  M=1,0
      K=1
      IF(S,LE,5,0E-07) GO TO452
      S=S/10,0
 452  CALL YVALUE(XMIN,MR,U,YA,COS,J,T)
      Y(K)=YA
      DO 78 I=1,N
 78   B(I,K)=XMIN(I,J)
 222  K=K+1
      IF(K,GT,KMAX)GO TO 900
      DO 50 I=1,N
      XMIN(I,J)=XMIN(I,J)+M*S*V(I,J)
 50   B(I,K)=XMIN(I,J)
      CALL YVALUE(XMIN,MR,U,YA,COS,J,T)
      Y(K)=YA
 633  FORMAT(20X,3(F10,7,5X),F12,5)
      K1=K-1
      IF(M2*(Y(K)-Y(K1)))37,902,31
 37   IF(K,GT,2)GO TO 44
      M=-M
      K=K+1
```

```
      DO 30 I=1,N
C      INCREASING THE POINTS  BY ONE STEP
C     XMIN(I,J)=XMIN(I,J)+2.*M*S*V(I,J)
   30  B(I,K)=XMIN(I,J)
      CALL YVALUE(XMIN,MR,U,YA,COS,J,T)
      Y(K)=YA
C
C     SUCCEEDED THIS WAY
C
C     TESTING THE SUCCESS OF THE STEP CHANGE
      IF (M2*(Y(K)-Y(K-2)).GT.0.) GOTO 32
C
C     FAILED BOTH WAU(31) - SPECIAL QUADRATIC FORMULA
C
      IF (Y(K-1)-2.*Y(K-2)+Y(K).EQ.0.) GOTO 812
      FUM=(Y(K)-Y(K-1))/(2.*(Y(K-1)-2.*Y(K-2)+Y(K)))
      JB=K1
      GOTO 3594
   32 CONTINUE
C
C     PUT NEW TRY INTO POSITION TWO
C
      Y(K-1)=Y(K)
      DO 34 I=1,N
   34 B(I,K-1)=B(I,K)
      K=K-1
C
C     NOW DOUBLE STEP SIZE AND CARRY ON
C
   31 M=2.0*M
      GO TO 222
   44 M= M/2.0
      K=K+1
      IF(K.GT.KMAX)GO TO 900
      DO 60 I=1,N
      XMIN(I,J)=XMIN(I,J)-M*S*V(I,J)
   60 B(I,K)=XMIN(I,J)
      CALL YVALUE(XMIN,MR,U,YA,COS,J,T)
      Y(K)=YA
      IF(M2*Y(K-2).GE.M2*Y(K)) GO TO 444
      SAM=Y(K)
      Y(K)=Y(K1)
      Y(K1)=SAM
      DO 666 I=1,N
      BON=B(I,K)
      B(I,K)=B(I,K1)
  666 B(I,K1)=BON
      GO TO 555
  444 Y(K1)=Y(K-2)
      Y(K-2)=Y(K-3)
      DO 777 I=1,N
      B(I,K1)=B(I,K-2)
  777 B(I,K-2)=B(I,K-3)
  555 G=-M2*90000000.0
      DO80 I=K-2,K
      IF(M2*G.GE.M2*Y(I)) GO TO 80
      G=Y(I)
      JB=I
   80 CONTINUE
```

```
      GO TO 732
  902 JB=K-1
      IF(K.LE.2) GO TO812
  732 IF(2*(Y(K-2)-2*Y(K-1)+Y(K)).EQ.0.0) GO TO 812
      FUM=(Y(K-2)-Y(K))/(2*(Y(K-2)-2*Y(K-1)+Y(K)))
      GO TO 3594
  812 FUM=0.0
 3594 DO 90 I=1,N
      XMIN(I,J)=B(I,K1)+M*S*FUM*V(I,J)
   90 CONTINUE
      DO 705 I=1,N
      IF(ABS(XMIN(I,J)-P(I,JB)).GT.Q)   GO TO 100
  705 CONTINUE
      CALL YVALUE(XMIN,MR,U,YZ,COS,J,T)
      YR=Y(JB)
      IF(M2*YZ.GE.M2*YR)GO TO 120
       YZ=YR
      DO 206 I=1,N
  206 XMIN(I,J)=B(I,JB)
  120 RETURN
  900 CONTINUE
      IF(IP.GE.1)WRITE(2,999)
  999 FORMAT ('0',10X,'YOU HAVE RUN OUT OF SPACE IN CAMPEY'//)
      STOP
      END
      FINISH
```

PURIFICATION OF WET-PROCESS PHOSPHORIC ACID BY SOLVENT EXTRACTION

WATER-PHOSPHORIC ACID- SOLVENT

BASIC DATA,PARAMETERS AND INDEPENDENT VARIABLES

BASIS OF DESIGN AND COST EVALUATION: 100 TONS P2O5/DAY

	IPE	ALCOHOL	MIBK	TRP
IMP.CONCN.IN INITIAL EXTRACT(CIY1)%	1.00000	1.00000	1.00000	1.00000
IMP.CONCN.IN FINAL PRODUCT(CIXP)%	0.10000	0.10000	0.10000	0.10000
IMP DIST.COEFF.(PURN.STEP)(MI)	10.00000	3.00000	5.00000	12.00000
IMP.CONCN.IN FINAL EXTRACT(CIYC)%	0.05000	0.05000	0.05000	0.05000
H3PO4 DIST.COEFF.(SLOPE ME)	2.50000	0.83000	1.97400	0.15800
H3PO4 CONCN.,TONS/TON FEED,(XF)	3.00000	1.85700	1.85700	3.00000
H3PO4 CONCN.,TONS/TON PRODUCT,(XP)	3.00000	1.85700	1.85700	3.00000
H3PO4 DIST.LINE INTERCEPT(B*)	-5.12000	-0.48100	-2.40800	0.00000
PRODUCT FLOWRATE TONS/DAY(P)	46.00900	74.32300	74.32300	46.00900
FEED DENSITY,TONS/C.M	1.60000	1.47000	1.47000	1.60000
SOLVENT DENSITY,TONS/C.M	0.72500	0.81600	0.81600	0.99000
RES.TIME IN MIXER,DAYS	0.00694	0.00694	0.00694	0.00694
COST OF UNINSTALLED STANDARD STAGE#	19000.00000	19000.00000	19000.00000	19000.00000
CAPACITY OF STANDARD STAGE,C.M,	5.80000	5.80000	5.80000	5.80000
FACTOR TO CALC.INSTALLED STAGE COST	2.60000	2.60000	2.60000	2.60000
PAY OUT TIME,YEARS,	3.00000	3.00000	3.00000	3.00000
MAINT.ALLOWANCE FACTOR,10% CAPITAL	0.10000	0.10000	0.10000	0.10000
POWER CONS.IN MIXER,HP/C.M	1.00000	1.00000	1.00000	1.00000
PUMP OVERHEAD HEIGHT,M	3.00000	3.00000	3.00000	3.00000
ELECTRICITY COST,#/KWH	0.01500	0.01500	0.01500	0.01500
WORKING DAYS PER YEAR,DAYS	330.00000	330.00000	330.00000	330.00000
OVERALL STAGE EFFICIENCY	0.90000	0.90000	0.90000	0.90000
RAFF.TREAT.COST,#/TON	5.00000	5.00000	5.00000	5.00000
DENS.OF FINAL EXTRACT,TONS/C.M,	1.10000	1.10000	1.10000	1.30000
H3PO4 DIST.COEFF.(WASH.STEP,MW)	66.90000	7.00000	43.50000	6.33000
DENS. OF WATER,TONS/C.M.	1.00000	1.00000	1.00000	1.00000
SOLVENT LOSS FACTOR,%,(L)	0.00010	0.00010	0.00010	0.00010
COST OF SOLVENT,#/TON	313.60000	672.00000	515.20000	1792.00000
PRODUCT CONCN.COST,#/TON	5.00000	5.00000	5.00000	5.00000
LOW.H3PO4 CONCN.IN SOLVENT,TONS/TON	0.02200	0.04000	0.02900	0.02000
H3PO4 CONCN.IN SOLVENT(YS),TONS/TON	0.10300	0.25000	0.11000	0.03000
TEST FACTOR OF YS	0.02000	0.05000	0.02000	0.03000
PHASE RATIO IN PURN.STEP(KP)	0.30000	0.50000	0.30000	0.08000
PHASE RATIO IN EXTN.STAGE(RE)	1.00000	1.30000	1.30000	7.50000
H3PO4 CONCN.IN RAFF.(XN)TONS/TON	2.10000	1.00000	1.40000	0.20000

THE ANNUAL LABOUR COST IS CONSTANT =#24000

THE SOLVENT IS DI-ISOPROPYL ETHER(IPE)

THE INDEPENDENT VARIABLES AND PARAMETERS ARE

CASE NO.	YS	KP	RE	XN	XP	CIY1	LOSS/STAG*R
1	0.10300	0.24432	0.40006	2.52531	3.00000	1.00000	0.00010
2	0.08300	0.24432	0.40006	2.52531	3.00000	1.00000	0.00010
3	0.06300	0.24432	0.40006	2.52531	3.00000	1.00000	0.00010
4	0.04300	0.24432	0.40006	2.52531	3.00000	1.00000	0.00010
5	0.02300	0.24432	0.40006	2.52531	3.00000	1.00000	0.00010
6	0.02300	0.24355	0.40004	2.49919	2.50000	1.00000	0.00010
7	0.02300	0.24355	0.40004	2.49919	2.00000	1.00000	0.00010
8	0.02300	0.24355	0.40004	2.49919	1.50000	1.00000	0.00010
9	0.02300	0.19884	0.40001	2.47472	1.00000	1.00000	0.00010
10	0.02300	0.19884	0.40001	2.47472	0.50000	1.00000	0.00010
11	0.02300	0.24513	0.40001	2.48511	3.00000	1.00000	0.00020
12	0.02300	0.24513	0.40001	2.48511	3.00000	1.00000	0.00030
13	0.02300	0.24564	0.40001	2.45926	3.00000	1.00000	0.00040
14	0.02300	0.24564	0.40001	2.45926	3.00000	1.00000	0.00050
15	0.02300	0.25947	0.40001	2.43383	3.00000	2.00000	0.00050
16	0.02300	0.25947	0.40001	2.43383	3.00000	3.00000	0.00050
17	0.02300	0.25947	0.40001	2.43383	3.00000	4.00000	0.00050

THE NO. AND CAPACITIES OF STAGES ARE

CASE NO.	N1(EXTN)	N2(PURN)	N3(WASH)	Q1(EXTN)	Q2(PURN)	Q3(WASH)
1	1.08830	3.05364	0.76075	9.70997	3.03780	3.09516
2	1.04700	3.05364	0.82126	9.75115	3.01907	3.07804
3	1.00951	3.03364	0.90035	9.78357	2.99835	3.05912
4	0.96999	3.03364	1.01244	9.84216	2.98189	3.04407
5	0.92421	3.03364	1.20077	9.96054	2.97525	3.03801
6	1.06513	3.04213	1.13756	9.20620	2.82323	2.98680
7	0.97180	3.04213	1.08056	10.14781	3.01008	3.28785
8	0.86385	3.04213	1.01729	11.75220	3.34384	3.81016
9	1.00692	3.70990	0.93378	10.34535	2.95747	3.84479
10	0.83831	3.70990	0.83579	14.42643	3.88252	5.83057
11	1.20322	3.02481	1.19379	8.51361	2.72727	2.81075
12	1.13162	3.02481	1.19529	8.81331	2.77936	2.85834
13	1.34487	3.01954	1.19124	8.03087	2.64538	2.73555
14	1.29237	3.01954	1.19213	8.19929	2.67468	2.76231
15	1.50319	3.60024	1.18891	7.80417	2.66100	2.73879
16	1.45720	4.02286	1.18954	7.92368	2.68222	2.75809
17	1.42296	4.32327	1.19004	8.01814	2.69900	2.77334

THE FLOW-SHEET FLOWRATES AND CONCENTRATIONS

CASE NO.	Y1	XO	YC	B	R	A	F	W	P
1	1.2896	5.0000	1.2896	179.9527	25.1659	449.8196	424.6537	71.1749	46.0090
2	1.2578	5.0000	1.2578	181.3598	25.0107	453.3368	428.3261	71.0197	46.0090
3	1.2269	5.0000	1.2269	182.6134	24.8591	456.4704	431.6313	70.8481	46.0090
4	1.1936	5.0000	1.1936	184.3662	24.7027	460.8517	436.1490	70.7117	46.0090
5	1.1550	5.0000	1.1550	187.2518	24.6477	468.0649	443.4172	70.6567	46.0090
6	1.1999	2.5105	1.1984	174.1341	26.6570	435.2905	408.6335	81.8678	55.2108
7	1.1171	2.2050	1.0822	192.9267	33.1582	482.2672	449.1089	102.1717	69.0135
8	1.0188	1.9406	0.9321	224.7526	44.2017	561.8237	517.6219	136.2197	92.0180
9	1.0740	1.7287	0.9238	198.7214	40.9756	496.7926	455.8170	179.0026	138.0270
10	0.9382	1.6377	0.6459	279.1586	71.7229	697.8815	626.1586	347.7769	276.0540
11	1.3102	5.0000	1.3102	160.0384	22.6575	400.0872	377.4297	68.6665	46.0090
12	1.2743	5.0000	1.2743	165.6722	23.0903	414.1716	391.0813	69.0993	46.0090
13	1.3748	5.0000	1.3748	150.9639	22.0161	377.4014	355.3854	68.0251	46.0090
14	1.3518	5.0000	1.3518	154.1299	22.2599	385.3165	363.0566	68.2689	46.0090
15	1.4384	5.0000	1.4384	146.7024	23.2044	366.7481	343.5436	69.2134	46.0090
16	1.4208	5.0000	1.4208	148.9489	23.3895	372.3642	348.9746	69.3985	46.0090
17	1.4072	5.0000	1.4072	150.7247	23.5359	376.8036	353.2677	69.5449	46.0090

THE STEPS AND FINAL COST,#

CASE NO.	EXTN.COST	RAFF.LOSS	PURN.COST	WASH.COST	SOLV.LOSS	CONCN.COST	TOTAL COST
1	31127.737	5679.671	40729.665	10338.509	10103.343	0.000	121978.925
2	30028.895	5734.756	40566.077	11120.688	10222.391	0.000	121672.807
3	29016.460	5784.334	40384.787	12142.875	10380.422	0.000	121708.878
4	27989.000	5852.100	40240.355	13610.833	10633.885	0.000	122326.173
5	26876.233	5961.123	40182.058	16121.692	11107.262	0.000	124248.368
6	29420.602	5439.366	38942.864	15105.071	10501.754	113872.275	237287.933
7	28605.030	6046.497	40601.071	15273.154	11301.608	227744.550	353571.910
8	27976.948	7074.192	43476.245	15826.417	12723.463	341616.825	472694.091
9	30013.310	8147.111	48949.183	14613.069	12911.807	455489.100	592123.581
10	31026.799	8702.220	58432.782	17149.734	17282.400	569361.375	725955.310
11	31591.864	4971.310	37859.757	15237.466	19954.767	0.000	133615.164
12	30388.502	5176.085	38328.646	15424.142	30585.215	0.000	143902.590
13	33994.722	4640.646	37049.200	14939.065	38574.518	0.000	153198.152
14	33111.844	4755.714	37315.612	15045.138	48771.976	0.000	163000.283
15	37294.816	4465.019	44346.654	14921.294	53072.118	0.000	178097.902
16	36513.403	4544.485	49809.240	14997.560	57115.663	0.000	186980.351
17	35931.506	4608.881	53746.323	15057.714	60107.362	0.000	193451.785

THE SOLVENT IS N-AMYL ALCOHOL

THE INDEPENDENT VARIABLES AND PARAMETERS ARE

CASE NO.	YS	KP	RE	XN	XP	CIY1	LOSS/STAG*B
1	0.25000	0.42851	1.20484	1.03214	1.85700	1.00000	0.00010
2	0.20000	0.41196	1.20486	0.99124	1.85700	1.00000	0.00010
3	0.15000	0.42168	1.20482	0.95394	1.85700	1.00000	0.00010
4	0.10000	0.43053	1.20482	0.91425	1.85700	1.00000	0.00010
5	0.05000	0.43885	1.20494	0.87454	1.85700	1.00000	0.00010
6	0.05000	0.43885	1.20494	0.87454	1.35700	1.00000	0.00010
7	0.05000	0.41262	1.20490	0.81474	0.85700	1.00000	0.00010
8	0.05000	0.45533	1.20490	0.86105	1.85700	1.00000	0.00020
9	0.05000	0.43533	1.20490	0.86105	1.85700	1.00000	0.00030
10	0.05000	0.43241	1.20490	0.84972	1.85700	1.00000	0.00040
11	0.05000	0.43241	1.20490	0.84861	1.85700	1.00000	0.00050
12	0.05000	0.43241	1.20490	0.84861	1.85700	2.00000	0.00050
13	0.05000	0.43241	1.20490	0.84861	1.85700	3.00000	0.00050
14	0.05000	0.43241	1.20490	0.84861	1.85700	4.00000	0.00050

THE NO. AND CAPACITIES OF STAGES ARE

CASE NO.	N1(EXTN)	N2(PURN)	N3(WASH)	Q1(EXTN)	Q2(PURN)	Q3(WASH)
1	5.44720	10.42244	1.03878	20.64028	15.24201	13.96212
2	5.06947	11.68554	1.18791	14.42838	10.67648	9.97127
3	4.66200	10.89117	1.38816	12.65451	9.51142	8.91997
4	4.40012	10.28984	1.68261	11.08860	8.47203	7.98629
5	4.18346	9.77465	2.21320	9.81065	7.62140	7.22283
6	3.01832	9.77464	1.92780	12.68909	9.28503	9.12749
7	3.82789	11.62649	1.57740	12.73985	9.05092	9.72424
8	4.49979	9.97936	2.20288	9.40201	7.33319	6.97453
9	4.40495	9.97955	2.20582	9.47611	7.37830	7.01425
10	4.79663	10.15745	2.19447	9.08487	7.10963	6.78193
11	4.76792	10.15745	2.19524	9.10342	7.12088	6.79184
12	4.50826	12.77796	2.20263	9.28395	7.23028	6.88826
13	4.33020	14.32157	2.20822	9.42260	7.31431	6.96231
14	4.21615	15.41969	2.21205	9.51875	7.37258	7.01367

THE FLOW-SHEET FLOWRATES AND CONCENTRATIONS

CASE NO.	Y1	XO	YC	B	R	A	F	W	P
1	0.9346	1.8570	0.9346	945.1256	274.1162	784.4398	510.3236	348.4592	74.3230
2	0.9186	1.8570	0.9186	673.8145	186.4050	559.2465	372.8415	260.7280	74.3230
3	0.8995	1.8570	0.8995	602.9439	169.0414	500.4424	331.4010	243.3644	74.3230
4	0.8825	1.8570	0.8825	539.2663	152.9063	447.5902	294.6839	227.2293	74.3230
5	0.8654	1.8570	0.8654	487.2247	139.6043	404.3560	264.7517	213.9273	74.3230
6	0.6940	1.3724	0.6892	653.6148	206.1568	542.4459	336.2891	307.8648	101.7080
7	0.6060	0.9911	0.5582	682.1358	243.4197	566.1327	322.7131	404.4673	161.0476
8	0.8766	1.8570	0.8766	466.9226	133.5120	387.5184	254.0065	207.8350	74.3230
9	0.8734	1.8570	0.8734	470.6027	134.3331	390.5727	256.2396	208.6561	74.3230
10	0.8860	1.8570	0.8860	451.1724	128.7868	374.4470	245.6602	203.1098	74.3230
11	0.8851	1.8570	0.8851	452.0941	128.9905	375.2119	246.2214	203.3135	74.3230
12	0.8769	1.8570	0.8769	461.0593	130.9722	382.6525	251.6803	205.2952	74.3230
13	0.8707	1.8570	0.8707	467.9450	132.4943	388.3673	255.8730	206.8173	74.3230
14	0.8666	1.8570	0.8666	472.7201	133.5499	392.3303	258.7805	207.8729	74.3230

THE STEPS AND FINAL COST,#

CASE NO.	EXTN.COST	RAFF.LOSS	PURN.COST	WASH.COST	SOLV.LOSS	CONCN.COST	TOTAL COST
1	254510.379	4048.265	399745.036	37628.020	393761.579	0.000	1113693.279
2	187610.569	2771.745	355478.393	34562.485	297902.494	0.000	902325.687
3	158409.559	2386.969	307309.409	37563.784	251689.565	0.000	781359.286
4	137192.821	2046.051	269277.252	42370.351	217550.869	0.000	692437.343
5	120445.550	1768.151	238773.169	52203.558	194140.044	0.000	631330.451
6	102741.796	2432.344	271515.116	52952.989	237078.966	113864.694	804585.905
7	130637.136	2306.261	317634.379	45151.277	286267.114	227729.388	1033725.555
8	126014.808	1668.361	237734.059	50790.715	383852.794	0.000	824060.736
9	123990.569	1689.095	238684.493	51046.614	577119.575	0.000	1016530.346
10	131360.812	1590.866	237149.477	49683.025	762553.371	0.000	1206337.551
11	130748.198	1596.077	237393.544	49747.649	953582.661	0.000	1397068.128
12	125217.696	1646.762	301616.969	50375.126	1107015.414	0.000	1609871.967
13	121438.184	1685.691	340604.687	50855.634	1202595.858	0.000	1741180.055
14	119023.726	1712.688	368621.755	51188.137	1272407.855	0.000	1836954.160

THE SOLVENT IS METHYL ISO BUTYL KETONE (MIBK)

THE INDEPENDENT VARIABLES AND PARAMETERS ARE

CASE NO.	YS	KP	RE	XN	XP	CIY1	LOSS/STAG*B
1	0.11000	0.33750	0.50665	1.47588	1.85700	1.00000	0.00010
2	0.09000	0.33750	0.50665	1.47588	1.85700	1.00000	0.00010
3	0.07000	0.33750	0.50665	1.47588	1.85700	1.00000	0.00010
4	0.05000	0.33211	0.50663	1.44868	1.85700	1.00000	0.00010
5	0.03000	0.33211	0.50663	1.44868	1.85700	1.00000	0.00010
6	0.03000	0.33211	0.50663	1.44868	1.35700	1.00000	0.00010
7	0.03000	0.29621	0.50660	1.41941	0.85700	1.00000	0.00010
8	0.03000	0.33305	0.50662	1.42990	1.85700	1.00000	0.00020
9	0.03000	0.33305	0.50662	1.42990	1.85700	1.00000	0.00030
10	0.03000	0.33305	0.50662	1.42990	1.85700	1.00000	0.00040
11	0.03000	0.33158	0.50660	1.41204	1.85700	1.00000	0.00050
12	0.03000	0.33158	0.50660	1.41204	1.85700	2.00000	0.00050
13	0.03000	0.33158	0.50660	1.41204	1.85700	3.00000	0.00050
14	0.03000	0.33158	0.50660	1.41204	1.85700	4.00000	0.00050

THE NO, AND CAPACITIES OF STAGES ARE

CASE NO,	N1(EXTN)	N2(PURN)	N3(WASH)	Q1(EXTN)	Q2(PURN)	Q3(WASH)
1	1,90236	5,03017	0,69997	14,48912	5,91262	5,84996
2	1,60651	5,03017	0,75850	15,36043	6,12014	6,03717
3	1,48233	5,03017	0,83746	15,46908	6,08851	6,00864
4	2,00632	5,14616	0,94927	12,11335	4,98094	5,01571
5	1,84470	5,14616	1,11508	12,15767	4,94239	4,98089
6	1,51261	5,14616	1,02411	14,65993	5,65823	5,94065
7	1,91419	6,17057	0,92873	13,56071	5,21635	6,13743
8	2,19181	5,12529	1,11317	11,16710	4,65897	4,72383
9	2,09523	5,12529	1,11364	11,41235	4,73078	4,78869
10	2,00653	5,12529	1,11411	11,66209	4,80391	4,85473
11	2,51405	5,16259	1,11184	10,45713	4,44036	4,52812
12	2,37306	6,51017	1,11238	10,71998	4,51714	4,59750
13	2,27542	7,30477	1,11279	10,92399	4,57673	4,65134
14	2,21333	7,87030	1,11307	11,06454	4,61778	4,68844

THE FLOW-SHEET FLOWRATES AND CONCENTRATIONS

CASE NO.	Y1	XO	YC	B	R	A	F	W	P
1	0.8622	1.8570	0.8622	401.5471	88.3337	792.5472	704.2135	162.6567	74.3230
2	0.8097	1.8570	0.8097	427.7117	91.4341	844.1892	752.7551	165.7571	74.3230
3	0.7792	1.8570	0.7792	432.7879	90.9616	854.2083	763.2468	165.2846	74.3230
4	0.8560	1.8570	0.8560	340.5119	73.4627	672.1124	598.6497	147.7857	74.3230
5	0.8261	1.8570	0.8261	343.4008	72.8942	677.8145	604.9203	147.2172	74.3230
6	0.7117	1.4621	0.6864	419.4080	101.1549	827.8398	726.6849	202.8629	101.7080
7	0.7266	1.2501	0.6183	391.7489	107.8924	773.2930	665.4006	268.9400	161.0476
8	0.8730	1.8570	0.8730	315.4176	68.8705	622.5904	553.7199	143.1935	74.3230
9	0.8610	1.8570	0.8610	322.3446	69.9320	636.2635	566.3314	144.2550	74.3230
10	0.8493	1.8570	0.8493	329.3986	71.0130	650.1870	579.1740	145.3360	74.3230
11	0.9083	1.8570	0.9083	295.3533	65.3749	583.0152	517.6402	139.6979	74.3230
12	0.8937	1.8570	0.8937	302.7774	66.5054	597.6700	531.1646	140.8284	74.3230
13	0.8829	1.8570	0.8829	308.5396	67.3827	609.0443	541.6615	141.7057	74.3230
14	0.8756	1.8570	0.8756	312.5092	67.9872	616.8801	548.8930	142.3102	74.3230

THE STEPS AND FINAL COST,#

CASE NO.	EXTN.COST	RAFF.LOSS	PURN.COST	WASH.COST	SOLV.LOSS	CONCN.COST	TOTAL COST
1	70601.335	5848.533	104162.791	14393.877	57896.211	0.000	276902.747
2	61932.140	6299.242	106527.545	15920.681	59751.301	0.000	274430.909
3	57407.630	6396.657	106168.957	17523.917	60090.707	0.000	271587.869
4	66265.780	4868.373	95313.764	17660.884	52114.540	0.000	260223.342
5	61072.784	4926.596	94833.192	20651.778	52583.805	0.000	258068.154
6	56567.038	6057.166	103558.906	21271.286	60870.700	113864.694	386189.790
7	68042.948	5488.118	117776.223	19703.645	66703.447	227729.388	529443.769
8	68659.087	4451.200	90888.118	19917.737	100462.686	0.000	308378.827
9	66568.512	4568.298	91797.219	20103.771	152247.871	0.000	359285.671
10	64654.914	4687.541	92718.038	20292.318	205243.218	0.000	411596.028
11	75456.895	4116.200	88727.578	19353.667	245167.575	0.000	456821.916
12	72385.445	4241.775	113147.371	19555.594	285857.707	0.000	519187.893
13	70264.115	4339.238	128044.979	19711.592	311621.204	0.000	557981.128
14	68918.059	4406.382	138761.969	19818.696	330498.965	0.000	586404.072

THE SOLVENT IS TRI-N-BUTYL PHOSPHATE (TBP)

THE INDEPENDENT VARIABLES AND PARAMETERS ARE

CASE NO.	YS	KP	RE	XN	XP	CIY1	LOSS/STAG*R
1	0.03000	0.08820	6.32916	0.69666	1.00000	1.00000	0.00010
2	0.03000	0.08482	6.32913	0.67661	0.50000	1.00000	0.00010
3	0.03000	0.07376	6.32947	0.68748	1.50000	1.00000	0.00020
4	0.03000	0.06374	6.32958	0.70549	1.50000	1.00000	0.00030
5	0.03000	0.05592	6.32912	0.72292	1.50000	1.00000	0.00040
6	0.03000	0.04843	6.32912	0.74035	1.50000	1.00000	0.00050
7	0.03000	0.03588	6.32975	0.94166	0.50000	2.00000	0.00050
8	0.03000	0.03204	6.32918	0.78332	1.50000	3.00000	0.00050
9	0.03000	0.02459	6.32918	1.01980	0.50000	4.00000	0.00050

THE NO. AND CAPACITIES OF STAGES ARE

CASE NO.	N1(EXTN)	N2(PURN)	N3(WASH)	Q1(EXTN)	Q2(PURN)	Q3(WASH)
1	3.13855	4.73252	3.05116	6.72949	5.20729	6.09611
2	2.53117	5.02215	1.75678	7.98630	6.05756	8.00032
3	3.89639	4.39954	4.66827	5.42531	4.22687	4.77980
4	3.82112	3.95209	4.57105	5.17551	4.00202	4.57005
5	3.73725	3.55392	4.50785	5.00400	3.84537	4.42418
6	3.65559	3.25958	4.45216	4.85262	3.70635	4.29481
7	2.09532	2.67510	1.65335	5.69808	4.15728	6.08205
8	3.45793	2.77925	4.34868	4.56188	3.43579	4.04338
9	1.98545	2.20186	1.63763	5.38912	3.88964	5.81164

THE FLOW-SHEET FLOWRATES AND CONCENTRATIONS

CASE NO.	Y1	XO	YC	B	R	A	F	W	P
1	0.2813	1.0070	0.2809	709.9604	40.1149	112.1730	72.0581	178.1419	138.0270
2	0.2247	0.5101	0.2240	866.2789	59.9921	136.8718	76.8797	336.0461	276.0540
3	0.3364	1.5059	0.3362	558.6615	22.0280	88.2636	66.2356	114.0460	92.0180
4	0.3413	1.5036	0.3412	531.0657	18.1625	83.9022	65.7397	110.1805	92.0180
5	0.3448	1.5032	0.3447	512.0724	15.4018	80.9074	65.5056	107.4198	92.0180
6	0.3479	1.5029	0.3479	495.2785	12.9338	78.2540	65.3201	104.9518	92.0180
7	0.2789	0.5061	0.2787	591.3264	18.0878	93.4202	75.3325	294.1418	276.0540
8	0.3542	1.5020	0.3542	462.9192	8.0341	73.1405	65.1064	100.0521	92.0180
9	0.2901	0.5045	0.2900	553.3907	11.7037	87.4348	75.7311	287.7577	276.0540

THE STEPS AND FINAL COST,#

CASE NO.	EXTN.COST	RAFF.LOSS	PURN.COST	WASH.COST	SOLV.LOSS	CONCN.COST	TOTAL COST
1	70700.853	390.732	90230.104	64453.393	509512.646	455489.100	1214776.828
2	63739.462	463.046	105653.516	44291.440	529933.349	569361.375	1337442.189
3	76292.116	303.398	73231.298	84177.149	951759.374	341616.825	1551380.160
4	72556.353	295.960	63487.608	80052.079	1292241.972	341616.825	1874250.797
5	69426.617	292.449	55314.058	77296.465	1585295.513	341616.825	2153241.927
6	66565.740	289.667	49503.482	74881.381	1846354.191	341616.825	2403211.286
7	42357.330	439.851	44051.149	34872.582	1247948.435	569361.375	1963030.723
8	60485.374	286.461	40428.015	70325.614	1609945.288	341616.825	2147087.577
9	38667.647	445.831	34721.795	33533.799	1058654.227	569361.375	1759384.675

EXECUTION ERROR 100 PROGRAM TERMINATED

THE OBJECT PROGRAM HAS REACHED AN END STATEMENT.

NOMENCLATURE

A	Interfacial area: sq.cm. Component A. Flowrate of A. Tons/day
A(h)	Energy needed to separate two droplets of unit radius from an initial distance h to infinite in equation (3.16): dyne cm.
a	Activity in equation (2.1). Interfacial area: sq.cm.
B	Component B. Flowrate of B: Tons/day
b	Intercept of equilibrium line. Annual maintenance cost as a fraction of equipment cost
C	Component C. Solute concentration, molar volume: gmoles/cu cm.
C_E	Annual cost of a real extraction stage including equipment and operating cost, £/year.
C_i	Concentration of impurity, weight fraction: Tons/Ton. Constant in equation (5.4).
C_p	Annual cost of a real purification stage including equipment and operating cost, £/year.
C_T	Total annual cost of a complete purification process, £/year.
C_v	Uninstalled cost of major equipment of an extraction, purification or washing stage, £/year.
ΔC	Concentration driving force, molar volume: gm.moles/cu
D	Component D. Distribution coefficient. Impeller diameter: cm.
D_D	Molecular diffusivity: sq.cm/cm.
d	Drop diameter: cm.

di	Individual drop diameter: cm.
d_{32}	Souter mean droplet diameter: cm.
E	Efficiency Energy input per unit mass and time = $N^3D^5\rho/M$.
E_M	Murphree stage efficiency,
E_o	Overall stage efficiency.
F	Feed Feed solution, B-free basis.
H	Height of mixing tank m. Time of operation, hr/year.
IPE	Isopropyl ether
K	Overall mass-transfer coefficient: g moles/(sec)... (sq cm)(g moles/cu cm).
k	Mass transfer coefficient: g moles/(sec)(sq cm).. (g moles/cu cm).
k_1, k_2..	Constants.
K_P	Phase ratio in the purification step = $R(1+X_o)/B(1+Y_1)$
L	Cost factor: £/ton.
l	Fraction of solvent flow lost/real stage: £/stage.
M	Mass of fluid in the mixer: gm.
MIBK	Methylisobutyl ketone
m	Any stage in the cascade. Equilibrium distribution coefficient, Y/X.
N	Agitator speed: rpm.
N_A	Mass transfer rate: g moles/(sec)(sq cm).
N_{Re}	Reynold number = $\rho_c VD/\mu_c$: dimensionless
N_{vi}	Viscosity group = $\mu_d/\sqrt{\rho_d \sigma D}$: dimensionless
N_{We}	Webber number = $\rho_c V^2 D/\sigma$: dimensionless.
n	Number of stages

P	Product
P	Product flowrate: Tons/day
P_A	Agitator power, input to agitator drive: hp/stage.
P_p	Pump power, input to pump drive: hp/stage.
p	(Cost of instruments, piping and installation as a fraction of major equipment cost) + 1.
Q	Volumetric flow rate: cu m/hr.
R_e	Phase ratio in the extraction step = B/A.
r	Droplet radius: cm.
Sc	Schmidt number = $\mu/\rho D$: dimensionless.
sh	Sherwood number = $k_c D/D_D$: dimensionless.
TBP	Tri-n-butyl phosphate.
t	Time: hours.
u	Velocity: cm/sec.
v	Velocity, impeller tip velocity: cm/sec. Drop volume:cu cm.
W	Water (component) Water flowrate: Tons/day.
X	Solute concentration in an aqueous phase:Tons/Ton
Y	Solute concentration in a solvent phase:Tons/Ton.

GREEK LETTERS

ϕ_D	Volume fraction of dispersed phase.
η	Microscale of turbulance: cm.
ε	Energy dissipation per unit mass
ρ	Density: g/cu cm.
$\Delta\rho$	Phases density difference: g/cu cm.
μ	Viscosity: poise = g/(cm)(sec)

ν	Kinematic viscosity: stoke = $cm^2/sec.$
σ	Interfacial tension: dynes/cm.
Γ	Surface force per unit area: dynes/sq.cm.
γ	Activity coefficient.
Δ	Difference
λ_n	Eigenvalue
β	Selectivity

SUBSCRIPTS

A,B,C,D	Components A,B,C,D.
c,e,f,m,n	Stages c,e,f,m,n,....
C,c	Continuous phase
D,d	Dispersed phase
E	Extract
F,f	Feed
I,i	Impurity
max	Maximum
min	Minimum
P	Product
R	Recycle stream
S	Solvent
*	Equilibrium value
i=1,2,etc.	Events 1,2,etc.
o	oil
w	water

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